Responses to reviewers

Indicated pages and lines refer to the untracked revised manuscript

Anonymous reviewer

Content

The article describes a very interesting passive approach to determine and couple interstitial water flow and nutrient transport in the hyporheic zone, the hyporheic passive flux meter (HPFM). The method is based on alcohol dilution from activated carbon and ion exchange resins. They firstly tested the ion exchange resins to obtain the most appropriate one. Secondly tested the HPFM in the field and compared the results with a most commonly used method such as pore water sampling. The presented approach is very interesting since it reduces temporal variability and the sampling effort, and it is very relevant because couples nutrients and water flow, to obtain hyporheic fluxes.

General comments

While interesting and novel, I have five major concerns as summarized herein.

First, I have concerns about the approach in the field test. The number and distribution of the HPFMs in the field seems to be done assuming a very homogeneous hyporheic zone, however this hardly ever happens. As a consequence the high spatial variability arises among all the measurements. There is not enough replication for basic statistical tests, and therefore, the comparison with the reference method, the pore water sampling (MLS), is very difficult to interpret. At least the analysis of the data should be done using those layers that have been measured as replicated presenting means and standard deviations/errors. And when possible perform statistical tests that proof or not the differences.

We agree that a much higher number of samplers would be needed to derive representative values. In general and especially for the calculations on uptake rates and denitrification potential we make it more clear in the revised version, that this study is mainly a method development and that the calculated rates are only an example for the use of HPFMs in exploring nutrient dynamics in the stream.

Where possible (e.g. experiments on triplicates, water quality parameters in table 4) we added standard deviation or ranges of values (table 3).

We did not aim to use MLS as a reference method to verify HPFM results, which is not possible because both method measure different things: MLS allow for snap shot sampling of pore-water CONCENTRATION, HPFM deliver average nutrient FLUXES over longer time periods.
We did want to compare the general characteristics of both methods, highlighting the benefits of time integrative measurements.
The revised version focuses more on the method development, also making this point clearer.

Second, the data from the HPFM should be explored with more detail and use the information provided by the coupled information to obtain more accurate information. In its present form the usage of the data is slightly superficial. A part of showing whether the HPFMs worked or not, the manuscript should also show which information can be obtained with them.

As mentioned above, the revised manuscript has a clear focus on the method evaluation. We agree that demonstrating the application of the HPFM and showing options on data treatment should be included. On the same time, it is true that we did not do enough repetitions to make robust statements about our study system. In the revised version we clarify that the field test should serve as an exemplary application in order to test the installation and retrieval procedure and the overall performance of the HPFM. We exemplarily show how the data can be used to interpret hyporheic nutrient dynamics, also adding a depths-wise calculation as suggested. Due to the lack of sufficient data, we don't want to go into too much detail here. We also focused introduction and discussion on the usage of hyporheic nutrient fluxes and why they are important. We think that from this point of view it should be clear, how HPFM data can be used.

Third, the growth of biofilm appears to be very significant in the HPFMs both in the laboratory columns and in the field. This could have strongly influenced the results and should be taken into account by the future or potential users of the HPFMs compared with other methods based on diffusion; however no data on this aspect are shown.

We admit that this topic was not represented adequately. We supply the results of the biofilm experiments as supplements (APPENDIX A). In general, the growth of biofilm on the resin granules and the failure to clearly quantify the (potential) effect of biofouling is the mayor limitation of the method and the major challenge for further improvement of the technique. We clearly state this now in the abstract and conclusion and suggest further steps in solving this problem and improve the performance of HPFMs. Also we added a few lines of discussion about potential effects from biofouling on resin/HPFM. Also see point 42.)

Fourth, while the abstract is quite direct, the introduction is too detailed what makes the reading confusing and lacks of a clear and direct objective. The methods section provides numerous and useful details as should be in a methodological manuscript, however they could be arranged in another way more intuitive that eases the reading. In general terms, the manuscript would be more convincing if it were presented as a comparison with MLS.

We edited the introduction, focusing more on the methodological part and clearly stating hypothesis and aims of the study.
The method section was rearranged. However, as mentioned above, direct comparison between MLS and HPFM measurements does in our opinion not make sense.

Fifth, the text is well written in general however a revision of expressions and grammatical mistakes is needed.

We corrected mistakes marked by you and other reviewers and double checked the revised version

Specific comments

1.) Page 1 Lines 25-27: In the manuscript, the HPFMs was placed in the streambed for a week and once recovered provided information on the total flux of nutrients and water during the study period however did not provide any information on temporal variability. In fact, pore water sampling could account for much more temporal variability than the presented approach.

Formulation corrected: "*Due to the high temporal variability of nutrient fluxes in the subsurface of our study reach, single grab samples of pore water could not be used to characterize overall fluxes. With HPFMs accumulative values for the average flux during the complete deployment time could be captured, while on the same time reducing the sampling effort." P1 L24ff*

2.) Page 1 Lines 9-33: The abstract or the keywords should provide some more detailed information about the method; more specifically include the use of resins and activated carbon.

Both were added to the key words and included in the abstract "*Their functioning is based on accumulation of the substances on a sorbent and concurrent dilution of a resident tracer which is previously loaded on the sorbent." P1 L17ff*

3.) Page 1 Line 15: it is not clear the meaning of the term load, does it refer to nutrient concentration?

Changed to "*fluxes of target solutes and water through those ecosystems." P1 L17*

4.) Page 2 Lines 13-14: The definition of hyporheic zone excluded groundwater, however in line 20 (page 2) there is a reference to the significance of groundwater for nitrogen cycling in the hyporheic zone. I suggest expanding the definition, seeing for example Boulton, A. J.; Findlay, S.; Marmonier, P.; Stanley, E. H.; Valett, H. M., The functional significance of the hyporheic zone in streams and rivers. Annual Review of Ecology and Systematics 1998, 29, 59-81.

Definition completed to "*The hyporheic zone, the subsurface region of streams and rivers that exchanges water, solutes and particles with the surface (Valett et al., 1993) and may mix stream-water during the transport through the sediments with underlying groundwater (Triska et al., 1989; Fleckenstein et al., 2010;Trauth et al., 2014)" P2 L11*

5.) Page 2 Line 29: In the discussion, the term hotspot has been used, I suggest keeping the term uniform and use it here as well.

We don't see how this word fits into here, or how this paragraph is referring to a hotspot. However, this paragraph was edited and reformulated

6.) Page 2 Line 35: Does "exchange rates" correspond to water, nutrients or both?

Water and solutes as clearly stated in the sentence before. *P3 L2*

7.) Page 4 Line 32: In the present study biofouling is also not clearly regarded since no control or no data are shown.

We reformulated the paragraph, stating that biofouling was considered as a potential challenge in our application. We also extended discussion on biofouling and provide the results from the experiments as supplementary material. Please see my comment above.

8.) Page 5 Lines 2-13: Please include information about the resin and AC such as pore size, specific surface, porosity... Please include also an estimation of the maximum potential adsorption, how much mass of the studied nutrient can be measured? Which is the detection limit of the HPFMs for nutrient and which is the minimum Darcy velocity that can be detected?
Please indicate in this section as well that resin and AC aimed to inform about two different parameters/processes.

Information about resin (P6 L14ff) and AC (P7 L4f) were added to the respective paragraphs. Detection limit for nutrient accumulation on the resin was included in the methods "*The limit of quantification LQ for the nutrient extraction resulting from this background was calculated according to the EPA Norm 1020B (Greenberg et al., 1992) as the sum of background concentration and 10 times the standard deviation and amounted to 24 µg NO3- g-1 resin and 0.097 µg PO4- g-1 resin*." P6 L9ff
An estimate of an overall detection limit is provided now in the discussion: "*As the values derived from the control incorporate all the processing steps of HPFMs and samples, they can be regarded as the method detection limit MDL (Greenberg et al.,1992). The MDL defines the lower limit for the use of HPFMs in cases were nutrient fluxes are very low and deployment time cannot be extended*" P14 L31ff

We clarify the different aims of resin/AC: "*was filled with a mixture of a macroporous anion exchange resin as a nutrient absorber and alcohol tracer loaded activated carbon (AC) for the water flow quantification.*" P5 L7

9.) Page 5 Lines 11-12: Why was this mesh size selected? Taking into account the characteristics of the streambed sediment, of the resin and/or AC, or both? Very fine streambed sediment could clog the mesh, or even enter the resin and AC and clog it. On the other hand, in a very permeable streambed the HPFM would probably act as an impermeable layer and limit the exchange of tracer and nutrients to diffusion. See Ward, A. S., et al. (2011). "How can subsurface modifications to hydraulic conductivity be designed as stream restoration structures? Analysis of Vaux's conceptual models to enhance hyporheic exchange." Water Resources Research 47: W08512.

We completed the method section on the selection of mesh size
"*In general, meshes should be as wide as possible because very fine mesh may act as a barrier to water flow limiting infiltration of water and solutes into the HPFM (Ward et al., 2011). However, the mesh should be smaller than the finest sediments, AC or resin granules." P5 L14f*
We did not observe neither clogging nor infiltration of fine particles. We agree that this is an issue which should be regarded and included it into our discussion "*If fine particles are observed to bypass the mesh and enter the HPFM a finer mesh should be chosen. We did not observe clogging of the mesh or intrusion of particles at our study, though in highly permeable systems with fine particle transport this might have to be considered.*" P16 L5ff

10.) Page 5 Line 4: Please indicate that the tracer loaded carrier is the activated carbon (AC).

Completed: "*The Hyporheic Passive Flux Meters (HPFMs) consisted of a nylon mesh which was filled with a mixture of a macroporous anion exchange resin as a nutrient absorber and alcohol tracer loaded activated carbon (AC) for the water flow quantification*." P5 L7

11.) Page 5 Lines 34-35, Page 6 lines 1-6: Were the HPFMs stored dry? When placing the HPFMs in the streambed there was a first wash of the resin and AC, could it be estimated how much is this first contact with stream water influencing the final result? How much of the maximum potential adsorption/dilution (%) is lost in this first step?

Yes, they were stored dry. "*HPFMs were built, stored dry and…" P9 L21*
We moved this section to a later part where it makes more sense and is better understandable. A "Flush" should be avoided by the deployment procedure. We clarified this in the respective paragraph! "*The diameter of the steel tube for installation tightly fitted with the rubber washers at the top and bottom end of the HPFM, so that vertical water flow through tube and HPFM during installation was inhibited.* " P9 L26
In addition a control HPFM was built to assess the potential loss/nutrient accumulation during deployment and retrieval. "*One additional HPFM with alternating layers was used as a control HPFM, in order to assess potential tracer loss or nutrient contamination during storage, transport and deployment/retrieval*." P10 L17ff

12.) Page 6 Line 14: The heading of this section is confusing since it is commonly placed at the end of the methods section; however this is a methodological manuscript. This section would be better merged with the correspondent method, Section 2.2.1 included right after the description of the AC, and section 2.2.2. merged with the description of the resins.

We rearranged the method section

13.) Page 7 Lines 4-6: Is "*JN*" time-averaged advective horizontal nutrient flux? Please indicate it together with the correspondent units.

completed "*time-averaged advective horizontal nutrient flux J_N (mg m² d^{-1}) can be calculated*" P8 L24

14.) Page 7 Line 10: The heading of section 2.3. is a bit confusing, does not reflect the aim of the section, to ease the reading, it might be better to swift this section to right after section 2.1.1.

As mentioned above, the method section was rearranged

15.) Page 7 Line 11: If as indicated experiments described in that paragraph were accomplished on triplicate; please present the data as means +/- standard error, or standard deviation.

std deviations or ranges were added in the text and tables

16.) Page 7 Lines 16-29: Please, provide more details on the experimental setup, for instance were the columns pump bottom-top or top-bottom direction, where the columns placed vertically or horizontally, for how long were the tests run. Please provide the brand of the pump.

We added information to this paragraph "… *placed in a vertical position and infiltrated with water collected from the study reach. … in order to ensure uniform infiltration at the surface of the column. Water was continuously pumped (peristaltic pump, ISMATEC® BVP Standard, ISM444) through the columns from top to bottom for 22 days at a speed of 20 mL* h^{-1}*, which also equals the expected Darcy velocity of* $q_x = 4$ *m* d^{-1}*. River water was supplied from a 22 L HDPE canister (Rotilabo® EPK0.1). SRP and* NO_3^- *concentrations in this reservoir were revised daily. The draining water at the bottom outlet of the columns was sampled twice a day and analyzed for SRP and* NO_3^-*"* P6 L21ff

17.) Page 7 Line 19: I wonder whether at the same nutrient flux into the HPFMs (high concentrations and low flow, or low concentrations at high flow) the differences in interstitial velocity (i.e. Darcy velocity) would influence the adsorption/dilution due to turbulent flow and finer diffusive boundary layer.

We do not think so and laboratory experiments I earlier studies, did not indicate that there are biases in this direction (see Cho et al. 2007). However, a validation on "field-behavior" should be conducted as soon as more measurements during different flows (especially low darcy flows) are available.

18.) Page 7 Lines 30-32: Please provide these results.

We provide the results in the supplement (APPENDIX A) and indicate that those supplements exist at the relevant point in the results section

19.) Page 8 Lines 1-2: The lower or higher concentrations of N and P respectively contained after the incubation were used to correct the obtained data in the field experiment?

The control HPFM was used to correct the HPFM result, because the control also accounts for other methodological errors. "*The results from the control HPFM also include uncertainties arising from sample storage, analytical processing and the background concentration of nutrients on the resin. Measurements of the other HPFMs were corrected by subtracting the transport, storage and deployment related tracer loss and nutrient accumulation detected in the control*." P10 L20ff

20.) Page 8 Line 17: Does "stones" refer to Boulders or cobbles? Please specify. If possible, please provide information on the granulometry of the streambed.

Completed." *The sediments at the selected site are sandy with gravel and small cobbles. Sieving of sediment samples delivered the effective grain size* d_{10}*= 0.8 mm and a coefficient of uniformity* C_u *= 3.13. The effective porosity* n_{ef} *is 13 %. After Fetter (2001) the intrinsic permeability can be estimated to* $K_i = 96\ m^2$ *and the hydraulic conductivity to* $k = 81\ m\ day^{-1}$ *Clay lenses are present in the deeper sediments below 35 cm*." P9 L10ff

21.) Page 8 Line 33 Which is the reasoning for doing such combination of resin and AC? Would the results be more accurate in this way? If the aim is to test simultaneously both approaches, this arrangement does not seem appropriate since each layer is considered independent from the other one, and it is not clearly assumed that the streambed will have uniform nutrient concentrations or interstitial flows.

We tested two different approaches, both with inherent advantages and disadvantages. Depending on study site and research question the one or other might be preferable. We explain this in the discussion. There we also point out that the heterogeneity of the hyporheic zone has to be considered. P15 L3ff

22.) Page 9 Lines 5-7: Are the presented results corrected with this control?

Yes, see 19.)

23.) Page 9 Lines 19-20: it is not clear why the oxygen loggers had to be placed four weeks in advance for re-equilibration, while the HPFMs where placed without re-requilibration period. Would it be wise for future measurements to leave for example a perforated metal case in the streambed for certain period before placing the HPFMs? In this way, would the hyporheic zone be re-equilibrated after hammering the metal case in the streambed?

Different to the oxygen loggers or the MLS samplers the HPFM did not have an impermeable outer casing. Also the relation between installation time and measurement time is different. We explain this in the discussion

"*Unlike typical well screen deployments where PFMs (Annable et al., 2005; Verreydt et al., 2013) or SBPFM (Layton, 2015) have been inserted into a screened plastic or steel casing, our technique enabled the direct contact of the HPFMs with the surrounding river sediments. Thereby, the integration of the HPFM in the natural system is improved and the generation of artificial flow paths along the wall of the device is avoided. As a result, the disturbance created by the HPFM is low compared to other intrusive measurements of hyporheic flow like a piezometer or salt tracer injection. Additionally, the HPFMs include a measurement time that is long relative to the duration of the installation*"

P15 L32ff

24.) Page 9 Lines 21-37 and Page 10 Lines 1-3: The manuscript aims to compare the HPFMs with the pore water sampler (MLS), therefore this has to be clearly stated and well explained in the methods.

As mentioned above, the primary aim of the study was NOT to compare these two methods directly. However, we agree that the description of the MLS sampling was incomplete and added additional information to this paragraph (eg. extraction rate). For more detailed information please see the cited literature: Sänger and Zanke (2009)

"Per sampler and depths 10 mL of pore-water was manually extracted by connecting a syringe to the open end of the Teflon tube and slowly sucking up water at a rate of 2 mL min^{-1}. The 4 extraction depths were sampled successively, always starting with the shallowest depths and continuing with ascendant depths. Manual pore-water samples were taken on the 4th and 11th of June 2015, both times between 1 pm and 4 pm local time." P11 L20

25.) Page 9 Line 23 and figure 2: Why is the MLS A located so far (>2m) from the rest of the measurement points?

We actually had more samplers installed in a transect. Unfortunately, the others were destroyed by vandalism so that we had only those two left for the experiment.

26.) Page 10 Lines 1-3: Are the N and P data from June presented in the manuscript? Or for June just information on SO3 and B are provided? And data from N and P just correspond to October?

We admit the information was confusing and clarified this paragraph "*As NO_3^- and SRP concentrations in the pore water samples taken on June 4th and 11th 2015 were unexpected and inconsistent with results from the HPFMs, the sampling was repeated on the 8th of October. The aim of this repeated sampling was to investigate whether diurnal variations in subsurface NO_3^--N and SRP concentrations could explain the discrepancies between MLS and HPFM results. In October, both MLS were sampled twice, the first time in the early morning before sunrise and again in the early afternoon (around 2 pm). Those samples were analyzed for NO_3^-, SRP and SO_4^{2-}. Due to technical issues, B could not be measured in October*." P11 L31ff

27.) Page 10 Lines 4-13: The measurements presented here should have an appropriate heading as the MLS, oxygen profiles… or do these methods belong to the MLS?

We agree! "*Surface water chemistry*" P12L1

28.) Page 10 Line 7: Within the context of the manuscript it is also interesting to provide the detection limit.

The manufacturer supplies the detection limit of 0.03 mg L-1, which is noted in the article as "precision" for the Pro PS probe. We added a line on LOD definition, to avoid confusion on terms. *"Instrumental precisions refer to the limits of detection (LOD) as stated by the manufacturers" P5 L23*

Anyway, we are measuring at concentrations above 2 mg NO3 per liter, so we don't think that the detection limit of the sensor will be relevant in our study site.

29.) Page 10 Lines 10-13: Most of the parameters measured with the YSI probes are not provided in the results or tables. Please include them in a table, with mean and standard error or deviation for the incubation period.

We added table 4

30.) Page 10 Lines 12-13: Which is the relevance of Chlorophyll-a for the aim of the manuscript?

We agree that it does not make sense to mention parameters just because the probe can measure them. We deleted chlorophyll a from the article.

31.) Page 10 Lines 17-19: Indicate clearer, if correct, the abbreviations of all terms: "the proportion of surface water (QSW, m3 s-1) infiltrating…"

We clarified terms and completed units

32.) Page 10 Lines 17-19: Considering the interesting information about Darcy velocities in the hyporheic zone provided by the HPFM, it would be more accurate to calculate the proportion of infiltrated surface water from the cumulative QHZ for each layer, so the ratio will be ΔQHZ/QSW.

Since one of the advantages of the HPFM is that it can measure nutrients and Darcy velocities simultaneously and at different depths, the results will be more complete using an approach that includes that information.

We agree that this would deliver additional information and is a further option for future uses of HPFM (which we will discuss in the discussion section). We only have very few measurements, so that calculations of this kind would be speculative. However, we liked your idea and included an example for depths wise calculation of uptake rates to the discussion: "*Calculating $U_{NO3\text{-}HZ}$ in the same way for each single depth assessed with HPFM can deliver additional information about vertical gradients on nutrient processing rates and help to identify the most active depths in hyporheic zone. $U_{NO3\text{-}HZi}$ of a particular layer in the hyporheic zone can be derived by the differences in uptake rate between the regarded layer and the overlying layer. For instance the removal rates attributed to the different layers of HPFM L6 would be $U_{NO3\text{-}HZ15}$ = 567 mg NO_3^--N m^{-2} d^{-1} in the shallow layer (0 to 15 cm depths), $U_{NO3\text{-}HZ30}$ = 174 mg NO_3^--N m^{-2} d^{-1} in the layer from 15 to 30 cm depths and $U_{NO3\text{-}HZ45}$ = 256 mg NO_3^--N m^{-2} d^{-1} in the deepest layer from 30 to 45 cm depths. From this example one could conclude that the shallowest sediments are the most efficient ones in term of nitrate removal. While removal activity is first declining with depths it later increases again. This finding is consistent with the higher amplitudes of oxygen concentration in 45cm depths compared to 25 cm depths, also suggesting higher biotic activity at the deepest layer. Potential reasons for this pattern could be decreasing nitrate penetration with depths (lower uptake at the middle layer than the shallowest one) which is in the deepest parts counter balanced by increased residence time and stronger reducing conditions." P17 L37ff*

33.) Page 10 Line 18: I am not sure if the measured velocity in the HPFMs can be described as horizontal it could have also been diagonal. Of course according to the calculation it is horizontal but it confuses the reading especially when the results from the temperature show that there was a very strong vertical downwelling. Another term such as interstitial velocity may be more appropriate.

We agree, this term is misleading here and changed it to horizontal vector of the Darcy velocity. The angle of hyporheic flow was assessed as well. See section 3.2.1. Vertical Darcy velocity (q_y)

With this, vertical flow q_y was slightly lower than average horizontal flow q_x. Resulting from the relation between q_y and q_x the angle of hyporheic flow ($\tan\alpha = \frac{q_y}{q_x}$) was 32° downwards" P13 L22ff

34.) Page 10 Lines 20-21: Due to the lag between the water entering the hyporheic zone from the surface and the measurements in deeper layers, it is no easy to calculate the removal of any nutrient in the hyporheic zone. The N removal activity of the hyporheic zone, as calculated, seems to underestimate the capacity of the hyporheic zone. Considering the interesting information from each layer provided by the HPFMs, it would be interesting to take advantage of it and calculate the removal as something like what follows:
Since there is a quite strong vertical flow, we can assume that the concentration in one layer depends on the previous one. In this way, it can be calculated that the uptake at each layer results from the difference in fluxes (layery – layery +1). Of course, as indicated in the introduction, one has to take into account both flow and concentration, that is why it seems better to use the fluxes and not the concentrations. The combined uptake of all layers will provide the total uptake rate in the studied section of the hyporheic zone that can be then compared with the N flux from the surface water.
Additionally, it could be calculated the amount of N removed in the hyporheic zone to the flux of N in the stream to have larger scale information. This would answer the question of how much does the hyporheic zone removes from what is in the stream/ecosystem?

Please see point 32.)

35.) Page 10 Line 31: How could this influence the results? Please include some data.

Data are included in APPENDIX A which is indicated in this paragraph.
The impact of biofilm on the measurement is discussed in the discussion section.

36.) Page 11 Lines 33-34: See comment on page 5 lines 11-12, could this observation explain, at least partially, the measured darcy velocities (figure 3) in the deeper layers?

We do not think so. AC 4 and AC 2 do not look so different.
Clay will be definitely less permeable than the HPFM/mesh. However, you are right that a statement like this (if relevant) needs further discussion. Since we didn't see any effect of the clay lens we removed this statement from the article

37.) Page 12 Lines 4-7: The high variability between both measurements (A and B), the lack of

replicates and hence the lack of statistical tests, makes it difficult to draw such conclusions out of the presented data. The presented values represent very high spatial variability in the hyporheic zone, either due to heterogeneous flow or the presence of hotspot/moments during the day. A more cautious sentence should be used, and in the discussion refer to data from the literature.

We changed the formulation and added a sentence admitting, that the differences are high!
"*In the repeated manual pore-water samples taken in October (**figure 6**) NO_3^- concentrations were uniformly higher in the early morning than in the afternoon, whereas SRP behaved the other way round. This trend was consistent in both samplers even though the average concentration and distribution over depths differed between the samplers A and B." P13 L35ff*

38.) Page 12 Lines 8-9: Are these values means or just punctual measurements, standard deviations should be then provided. If enough data are available, a simple statistical test should be applied, for instance, one-way analysis of variance (ANOVA).

Continuous readings from sensors. We added table 4, including std, min and max values which we think is more informative here than a one way ANOVA

39.) Page 12 Lines 13-14: The temperature profiles provided information on vertical downwelling from the surface water. However, the darcy velocity obtained from the HPFMs was named as horizontal, however it is not possible to know which the actual direction of the water was. To avoid confusion with the fact that the flow was strongly vertical it might be better to name the flux obtained in the HPFMs as interstitial velocity and assume the sediment was isotropic.

What the HPFMs really measure is the horizontal vector of the interstitial flow. Likewise in the temperature profiling we assess the vertical vector of the interstitial flow. We clarified this in the method section, explaining the vertical flux measurements: "*The vertical vector of hyporheic Darcy velocities q_y were measured supplementary to the horizontal fluxes assessed with the HPFM in order to estimate the general direction of flow (upwards or downwards) and to calculate the angle of hyporheic flow*." P10 L27ff

40.) Page 12 Lines 19-23: Considering the high variability shown with two HPFMs in the manuscript, at least three per parameter should be placed in the streambed (flow or nutrients). Even in channelized rivers, small scale variability and heterogeneous residence time distribution occurs (see for example data from vertical water flux Mendoza-Lera, C. and M. Mutz (2013). "Microbial activity and sediment disturbance modulate the vertical water flux in sandy sediments."

Freshwater Science 32(1): 26-35.). Additionally, even if low variability is assumed, such approach would be statistically more consistent.

We agree and admit the lack of sufficient samples for quantitative statements at several points while underlining the need for a higher density of measurements "*Even in those systems, small scale variability in stream bed and sediment characteristics can cause spatially heterogeneous flow distributions (Lewandowski et al., 2011; Mendoza-Lera and Mutz, 2013). The second approach with alternating nutrient sorbents and water flux measuring segments is therefore preferable in most other cases as long as a high resolution over the vertical profile is not required. In general, several HPFMs should be grouped together in order to obtain representative results*." P15 L8ff

41.) Page 12 Lines 30-31: Data on substantial biofilm growth are not provided, please include.

See APPENDIX A

42.) Page 12 Lines 31-34: Not only biofouling could influence the results, what about uptake/release of nutrients by the biofilm? Right after placing the device in the streambed in was a sterile substrate, which informed about the nutrient concentration in the water flowing through it, and therefore about the surrounding conditions in the hyporheic zone. However, after certain time the HPFMs become an actual physical substrate where the microbial community developed, and therefore the HPFMs became part of the hyporheic zone. Therefore, the information provided by the HPFMs after the incubation also refers to the community inhabiting it.

That's correct! And an important issue which we incorporated in the discussion. As mentioned above, the biofilm growth on the resin granules remains the mayor limitation to the method which we did not outline that well before but make clear in the edited version.
"*We observed substantial biofilm growth on the resin in the laboratory and on the top 2 cm of the field-deployed HPFM R2. The results of the column experiments suggest that biofilm growth on the resin porous media did not affect its loading capacity and that biofilm growth only started after the loading capacity of the tracer was exhausted. R2 detected higher* NO_3^- *fluxes in the top layer than the other HPFM. This could be due to contamination of the top layer of this HPFM with surface water (if the HPFM was not introduced sufficiently deep into the sediments), this would further imply that this layer was exposed to much higher water and nutrient infiltration, so that the loading capacity was exhausted before the end of the experiment, thus allowing biofilm accumulation. At the current state it is unclear, to what extent the biofilm bound nutrients can be extracted by the procedure used here*" P15 L18ff

43.) Page 13 Lines 4-6: Please provide example of the intrusive measurements of hyporheic flow. As occurs when placing piezometers of smaller diameter than the HPFMs+metal case disturbance is created and likely after removing the metal casing fine sediment was sucked into the HPFMs as happens when placing piezometers. When the HPFMs were removed from the streambed and the measurements perform, was there evidence of fine sediment intrusion? Was there any evidence of clogging in the mesh?

We are more precise and carful on this comparison now.
We did not observe sediment intrusion, neither clogging of the mesh.(see also 19.) But we agree,that this is a point which should be considered and which we mention in the discussion. We also clarify that potential convergence or divergence into/around the device is accounted for in the equation and outline the limitations for this correction. Also see introduction "*Corrections for convergence and divergence of flowlines into or around the flux meter have been established in earlier studies (Klammler et al., 2004). However, accounting for an impermeable outer casing of a flux meter is much more complicated and requires additional factors which have to be determined experimentally for each specific application (Klammler et al. 2004, Annable et al. 2005, Hatfield et al. 2004). For hyporheic studies we therefore intended to deploy the passive flux meter in a way that allows direct contact with the surrounding sediments and minimal manipulation of the natural flow pattern*" P4 L27
and method section 2.5.2

44.) Page 13 Lines 11-17: It would be interesting to know which is the time scale detected by the method. If oscillation occurs within 12 hours or less, could the method be further adapted? For example placing the HPFMs for few hours?

We included a discussion on upper and lower limits "*The minimum and maximum deployment time will depend on the Darcy velocity and nutrient concentrations at a study site. As the values derived from the control incorporate all the processing steps of HPFMs and samples, they can be regarded as the method detection limit MDL (Greenberg et al.,1992). The MDL defines the lower limit for the use of HPFMs in in cases were nutrient fluxes are very low and deployment time cannot be extended. We recommend that a control HPFM be incorporated in each field application of HPFMs in order to determine the specific MDL. The upper limit is given by the loading capacity of the resin or complete displacement of all resident alcohol tracers.*" P14 L31ff

45.) Page 13 Lines 30-32: I am not sure whether such assertions can be done in the light of the limited replication and statistical tests. Since the difference in P concentration has not been proofed (no statistics) it is no possible to link the dynamics of phosphorous with oxygen. However, it could be interesting to take advantage of the oxygen profiles and determine if the dynamics observed in N and P in the HPFM and/or MLS correlate with the mean oxygen concentration.

We agree that this was rather speculative and reduced this statement to "*The redox conditions in the subsurface also regulate the mobilization/demobilization of phosphate (Smith et al., 2011). The repeated manual sampling of pore-water from MLSs in October showed diurnal variations of SRP and NO_3^- in the subsurface of the testing reach, supporting the hypothesis that diurnal cycles in benthic metabolism caused temporal variations in hyporheic SRP and NO_3^- concentrations at our study site*." P16 L22

We tried to assess the correlation between oxygen concentration and nutrient uptake by a bi-dial sampling of MLS, the results are discussed as indicated above

46.) Page 13 Lines 36-37: The HPFMs provide information of a flowpath, the length, velocity and residence time of the water before reaching the HPFMs is not known (further tracer tests could be implemented in combination with the HPFMs). Then it is difficult to determine whether there are hot spots for denitrification or hot moments, or both (see Abbott, B. W., et al. (2016). "Using multi-tracer inference to move beyond single-catchment ecohydrology." Earth-Science Reviews).
Additionally, downwelling into the hyporheic zone does not occur as a front but rather as semicircular flowpaths, see for instance:
Thibodeaux, L. J. and J. D. Boyle (1987). "Bedform-Generated Convective-Transport in Bottom Sediment." Nature 325(6102): 341-343.
Salehin, M., et al. (2004). "Hyporheic exchange with heterogeneous streambeds: laboratory experiments and modeling." Water Resource Research 40: W11504.
Rehg, K. J., et al. (2005). "Effects of suspended sediment characteristics and bed sediment transport on streambed clogging." Hydrological Processes 19(2): 413-427.\

We are more carful on our formulation now
"*We found continuously degreasing NO_3^- concentrations with depths, suggesting that this entire area (and potentially deeper) of the subsurface contained active sites for denitrification*" P17 L15

We are aware that (vertical) water flow will be heterogeneous and much more complex than a singular flow direction, however we think that our conclusion on the extension of the hyporheic

zone is still correct. We clarify that this is an assumption and suggest additional tracer tests to accomplish HPFM measurements. "*Conducting collateral tracer tests, as suggested for example by Abbott et al. (2016), could deliver further evidence and characterize distinct flow paths. Nevertheless, since vertical water movement was overall downward and the lowest concentrations of NO3- were observed in the deepest segments of the HPFM, it is very likely that the hyporheic zone at our study site extends deeper than the 50 cm evaluated*" P17 L19ff

47.) Page 14 Line 10: I suggest including in this section an summary in the form of a table of the factors that should be taken into account for applying the HPFMs in different contexts, for example pH should be taken into account in an acidic stream in a mining area, or permeability is to be taken into account to approximate the permeability of the studied reach (for instance the following method could be used to define the appropriate permeability in the HPFMs Datry, T., et al. (2014). "Estimation of sediment hydraulic conductivity in river reaches and its potential use to evaluate streambed clogging." River Research and Applications 31(7): 880–891).

The overall aim was to develop HPFMs which can be applied in a wide range of systems. Changing the sorbent would require to repeat a lot of analytical work on the new sorbent in order to identify the sorptive characteristics, retardation factors etc. The permeability of the HPFM (relative to the surrounding environment) is incorporated in the correction factor alpha. We recognize that this issue rose questions in the reader. We provide more information about this factor in the method section and added a line to the discussion. For more details please see the cited articles (Hatfield et al 2004, Annable et al 2005)
"*The correction for convergence of flowlines into the device or divergence around it is relatively simple and already incorporated in the equation for the flux calculation. We believe that it is applicable for a wide range of field conditions. However, for very coarse sediments, a protection of the HPFM with a screened plastic or steel casing might still be preferentia*l" P16 L3ff

48.) Page 14 Lines 2-5: I agree, the hyporheic zone is probably deeper than the scale of the HPFMs, however it is as well very heterogeneous in residence time distribution and therefore increasing the number of measurements and/or the scale will be a very interesting. This, together with the high variability of the provided data, indicates that future applications of HPFMs should have enough replicates.

Yes, we have to admit that!

"*Considering the high spatial heterogeneity of the hyporheic zone, a higher number of HPFM would be needed to derive reliable and statistically supportable rates of hyporheic nutrient dynamics. The following example aims to display further possibilities of interpreting HPFM measurements. At our study site,…*" P17 L24

49.) Page 15 Line 20: When more than one author it is uncommon to acknowledge in first person.

was changed

50.) Table 2: Please include either ranges or means +/- standard deviation.

completed

51.) Table 3: Please include either ranges or means +/- standard deviation.

completed where possible

52.) Figure 1: Please indicate to which approach corresponds the picture resin or AC, or alternating segments.

Figure capture improved

53.) Figure 2: For a non-german reader this map won't be very informative, especially because the aim of the manuscript is not to study that stream. I encourage presenting other information instead such as the temperature profiles.

We removed this map from the figure. However, we don't think that a grave of the temperature profiles is very informative. We reconsidered which results we would like to present as graphs and decided not to add another graph. We did supplement figure 1 in order to make the functioning principle of HPFM easily understandable.

54.) Figure 3: It might be more appropriate to express the fluxes per volume of sediment, in this way confusion with the denitrification rate units would be avoided. Additionally, in table 2, mass fluxes for nutrients are expressed with other units.

units corrected

55.) Figure 5: I am not familiar with the symbol for diameter to indicate mean concentrations, and it is a bit confusing. I suggest to simply adding surface water.
Considering the variability of the values measured in the hyporheic zone, it would be interesting to include the range of concentrations, or mean +/- standard error or deviation, of the surface water during the deployment time, as understood from the method the nutrient concentrations were measured every 15 mins.

Ø was replaced by “average”, min and max concentrations were added.

Technical corrections

56.) Page 2 Line 18: Correct phosphate, per phosphorous, or P per PO4-
57.) Page 3 Line 20: Correct technics, per techniques.
58.) Page 4 Line 34: Space missing in “…Pin…”
59.) Page 7 Line 35: Correct KCL per KCl
60.) Page 8 Line 13: Correct figure 2 instead of figure 3
61.) Page 10 Line 2: Correct sun rise, per sunrise
62.) Page 10 Line 20: Correct NO3-, per NO3--N
63.) Page 12 Line 4: Correct SRP, per SRP-P
64.) Page 12 Line 14: For which sentence stands the citation (Layton, 2015)?
65.) Page 14 Line 20: Correct hot spot, per

J. Lewandowski (Referee)

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Received and published: 20 September 2016

Vanessa Kunz and coworker present in the manuscript "Quantifying nutrient fluxes in Hyporheic Zones with a new Passive Flux Meter (HPFM)" a novel technique to measure horizontal water fluxes and nutrient fluxes in hyporheic zones. Without doubt this is an exciting technique to answer unsolved questions about transport and turnover in hyporheic zones. Up to now the lack of adequate techniques hindered in-depth investigations of transport and turnover in this important transition zone.

Dear Jörg Lewandowski,

thank you very much for your comments and suggestions! Your remarks contributed productively to the improvement of our article!
Please see below our responses to your comments.

Major comments

My major concern about this method is its impact on subsurface flow paths and flow velocities.
As a consequence the calculated loads might be misleading. Since the device will be placed in sediments with different hydraulic conductivities, its hydraulic conductivity will sometimes be larger than that of the rest of the sediment and sometimes smaller. In cases where the hydraulic conductivity is lower than that of the surrounding sediment most flow paths will bend around the device instead of passing it. As a consequence there will be much less uptake of nutrients and smaller flow rates. In the opposite case flow will be "sucked" into the device. Nutrient uptake and flow rates will be overestimated. This question could have been addressed in a lab experiment with a box filled with different sediment types with known horizontal flow and a HPFM placed in the center of the box. Alternatively, modelling would also be a method to address this problem. Even without additional investigations it is necessary to carefully discuss this shortcoming and even mention it in the abstract.

Potential convergence or divergence into/around the device is accounted for in the equation (2) for J_N with the correction factor α. We admit that this was not adequately presented in the original manuscript. We completed the method section on nutrient fluxes (Chapter 2.5.2.), explaining this correction factor and referring to literature for more detail:
P8 L27 ff "*…and α (-) is a factor ranging from 0 to 2 that characterizes the convergence ($\alpha > 1$) or divergence ($\alpha < 1$) of flow around the HPFM. If, like in the case presented here, the hydraulic conductivity*

of the HPFM sorbent (resin or AC) is much higher than of the surrounding and the HPFM is in direct contact with the sediments (i.e. in absence of an impermeable outer casing or well wall), α can be estimated after Strack and Haitjema (1981)

$$\alpha = \left(\frac{2}{1+\frac{1}{K_D}} \right) \quad (3)$$

where $K_D = k_D\, k_0^{-1}$ is the dimensionless ratio of the uniform hydraulic conductivity of the HPFM sorptive matrix k_D ($L\ T^{-1}$) to the uniform local hydraulic conductivity of the surrounding sediment k_0 ($L\ T^{-1}$). For more details on the correction factor α and applications where a solid casing is required or the permeability of the surrounding sediments is higher than of the device see Klammler et al. (2004) and Hatfield et al. (2004)"

We also discuss potential limitations for this correction, P16L3ff: "*The correction for convergence of flowlines into the device or divergence around it is relatively simple and already incorporated in the equation for the flux calculation. We believe that it is applicable for a wide range of field conditions. However, for very coarse sediments, a protection of the HPFM with a well screen might still be preferred.*
"

Background information on the correction is additionally presented in the revised introduction. P4 L27ff "*Corrections for convergence and divergence of flowlines into or around the flux meter have been established in earlier studies (Klammler et al., 2004). However, accounting for an impermeable outer casing of a flux meter is much more complicated and requires additional factors which have to be determined experimentally for each specific application (Klammler et al. 2004, Annable et al. 2005, Hatfield et al. 2004). For hyporheic studies we therefore intended to deploy the passive flux meter in a way that allows direct contact with the surrounding sediments and minimal manipulation of the natural flow pattern*"

Minor comments

1.) In general the paper is very well written and I could only identify a few typing and grammatical errors.

We corrected mistakes marked by you and other reviewers and double checked the revised version

2.) The only section of less quality is the abstract. I had the feeling that this was written in a hurry after finalizing the rest of the manuscript. However, as most central part of the manuscript it deserves more care to assure the high quality of the rest of the manuscript.

We edited the abstract concentrating more on the method development, also mentioning limitations (e.g. biofouling) of the method.

3.) The introduction is well written but relatively long. You might consider to slightly shorten it.

We condensed the introduction, focusing on the methodological aspect of this study. We therefore also added information where required (eg. on conversion/divergence of flow lines around the device)

4.) The material and methods section is also relatively long and sometimes a bit confusing. Consider to improve its structural elements.

As we focus mainly on the method development, it is inevitable that the method section is detailed and as a result long compared to the other sections. We recognized that the structure of this section was confusing to several reviewers and reorganized it.

5.) The results section is short. The discussion is very well written and of optimum length. The same applies to the conclusions section.

The aim of this study was not to characterize the processes at our study site, that's why we think that the presented results are sufficient. We also considered moving parts of the discussion (eg. the uptake calculations) or methods (the results from the background nutrient extraction) to the results, but finally decided that they were more appropriate at their current location

6.) The left part of Fig. 2 can be removed. I do not see any need for this figure and it is so small that it is impossible to see anything here. I recommend refering to another paper where such a map has been included instead of this one here.

We removed this part of the figure and referred to Kamjunke et al., 2013, where the study stream is explained in more detaile.

7.) P2L24ff: "In stagnant waters, such as lakes, the transport of dissolved nutrients to the sediments is dominantly controlled by diffusion. Therefore, surface water concentrations of nutrients are a good predictor for uptake processes and potential limitations (Dillon and Rigler, 1974;Jones and Bachmann, 1976)." Both sentences are completely wrong. Diffusion is only a relevant transport process over very short distances but not in a water body or as transport process from a lake to its sediment. Diffusion is a relevant process in the diffusive boundary layer above the sediment

surface. In the water body there are many active transport processes such as wind- and temperature-induced transport. You can also discuss this with the people at UFZ Magdeburg involved in lake physics. Transport of nutrients to the sediment occurs mainly in particulate (and not in dissolved) form. In lake sediments many different advective transport processes occur in addition to diffusion, for example groundwater discharge, wave- or seiches-induced pore water transport in the sediment and bioturbation. The latter is especially relevant in shallow lakes. For example, for Lake Müggelsee in Berlin it is well-known that chironomids pump the entire water body through the sediment once a week. Referring to the second of the above cited sentences: Nutrient concentrations in surface waters of lakes are mainly controlled by processes in the water column. For example SRP concentrations are controlled by the very efficient uptake of SRP by plankton during the growing season. That is the reason why SRP concentrations even in eutrophic lakes are usually low during the summer.

We agree you are right and deleted this paragraph, refocusing the introduction in general

8.) In the introduction I would expect a paragraph about hyporheic flow and methods to measure hyporheic flow. The HPFM aims on measuring water and nutrient fluxes but the introduction solely focusses on nutrient fluxes. Please add something about determination of hyporheic flow. For example the heat pulse sensor of Lisa Angermann could be mentioned here but also other methods. I know that the HPS did not work at your site but nevertheless you can mention that there is a device that can be used in finer sediments.

We completed the introduction P3 L23ff: "*Exchange rates are traditionally assessed via hydraulic head differences or tracer injections (USEP 2013, Fleckenstein et al. 2010). High resolution vertical temperature profiles have efficiently been used to derive vertical Darcy velocity (qy) (m d^{-1}) in the streambed. This method is based on time series measurements of temperature in the stream and in the sediments at several depths. Based on a numerical model, vertical flow velocities can then be calculated from the measured attenuation and phase shift of the diurnal temperature signal which, at depth, varies with the vertical hyporheic flux (Keery et al. 2007, Schmidt et al. 2014). While measurements of vertical Darcy velocities are a valuable asset and have been used as supplement in this study, horizontal fluxes are also needed in order to assess hyporheic transport and residence time (Binley et al. 2013, Munz et al. 2016). Active heat-pulse tracing enables highly resolved in situ measurements of direction and velocity of hyporheic flow (Lewandowski et al., 2011; Angermann et al., 2012). These methods are valuable in shallow sediments (max.15-20cm) and rivers with fine sediments, but may not be implementable in streams with coarser sediments*."

9.) In general I think you consider the sediment only as a sink and not of a source of nutrients. For example in line 11 on page 1 you write “nutrient removal” although the hz is sometimes a source. Besides a temporary storage (e. g. uptake and later release of nutrients) the transport of particulate organic matter to the sediment surface should also be considered. Once this organic material is buried it can release nutrients as a consequence of mineralization processes. Keep this in mind throughout your manuscript.

We changed formulations to “*nutrient processing*” were adequate. While of undeniable importance, particulate organic matter transport was not in the scope of our study (because only solutes are assessed with our methods). With the aim of condensing the introduction to the points really relevant for HPFM measurements, which is hyporheic solute fluxes, we decided to exclude these points from our article.

10.) The sediment description on page 8 is quite poor. It would be great to know a little bit more about the grain distribution or hydraulic conductivity of the sediment.

We completed the description of the sediment characteristics P9 L10ff “*The sediments at the selected site are sandy with gravel and small cobbles. Sieving of sediment samples delivered the effective grain size d_{10}= 0.8 mm and a coefficient of uniformity C_u = 3.13. The effective porosity n_{ef} is 13 %. After Fetter (2001) the intrinsic permeability can be estimated to K_i = 96 m² and the hydraulic conductivity to k = 81 m day^{-1} Clay lenses are present in the deeper sediments below 35 cm*.”

11.) P12L19ff I do not see the usefulness of this device. I think there is always much more small scale variability in hyporheic zones than assumed. Even in channels. I would recommend placing two alternating HPFMs in the sediment instead and place them with a small depth variation. In that case you will end up with the same spatial resolution but you can assure that flow and nutrient fluxes match to each other. Also, in the entire paper I have not understood the motivation for the separated HPFMs.

We evaluated two different approaches to construct HPFMs in a way that separates resin and AC and thereby prevents the nutrient background on the AC from biasing the results. We added an explanation to the revised article
P15 L3 ff “*The high nutrient background on the AC required the separation of resin and AC in the HPFMs. We tested two different HPFM designs in this study, of which each inherits designated characteristics being more or less beneficial for different specifications:”*

We believe that both approaches have advantages and disadvantages. "The first approach, pairs of two HPFMs where one is used to assess the water flux and the second to capture nutrients is preferable if a high resolution depth profile is needed (a heterogeneous horizontal flux in the vertical direction). Since this approach assumes that local horizontal heterogeneity is negligible in the range of 20-30 cm, we recommend this type for use in uniform systems such as channelized river reaches."

However we agree that the local heterogeneity of stream beds/hyporheic flow should be considered and mentioned at this point: P 15 L3ff "*Even in those systems, small scale variability in stream bed and sediment characteristics can cause spatially heterogeneous flow distributions (Lewandowski et al., 2011; Mendoza-Lera and Mutz, 2013)*."

Summarizing, I recommend accepting the manuscript after minor revision.

Jörg Lewandowski, IGB Berlin

Please also note the supplement to this comment:

http://www.biogeosciences-discuss.net/bg-2016-334/bg-2016-334-RC3-supplement.pdf

Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-334, 2016.

J. Rozemeijer (Referee)

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Review of Kunz et al, Quantifying nutrient fluxes in Hyporheic Zones with a new Passive Flux Meter (HPFM).

The paper presents a useful monitoring tool to increase our understanding of nutrient cycling in the hyporheic zone of streams. The paper is very well organized and written. I only have some minor comments that could be considered by the authors.

Dear Mr. Rozemeijer,

thank you for your comments! We appreciate that you liked our article. However, for most other reviewers, the structure of the article was confusing, that's why we rearranged several parts of it. Especially the methods section.

We improved our article, also taking in account your suggestions.
Please see below our comments to your specific remarks.

P5 l6: From figure 1 the idea of tracer release and nutrient absorption is not immediately clear. Also, the difference between the sections filled with tracer and with absorber is not clear in the graphic (same color)

We improved and supplemented Figure 1.

P6 l32 and P7: "if not indicated otherwise" Remove?

This phrase was removed

P9l8: At this point in the paper it is not clear why these additional measurements are also done. Consider adding a short introduction.

We added a sentence or two to each of the sub-paragraphs briefly explaining the goal of each measurement:

P10 L27ff "*The vertical vector of hyporheic Darcy velocities q_y were measured supplementary to the horizontal fluxes assessed with the HPFM in order to estimate the general direction of flow (upwards or downwards) and to calculate the angle of hyporheic flow*." …
P11 L6ff "*We monitored the subsurface oxygen concentration as a primary indication on the redox status of the hyporheic zone in order to evaluate the potential for NO_3 reduction and PO_4 mobilization." …*
P11 L13f *"Pore-water nutrient concentrations were measured to substantiate the HPFM results." …*
P12 L2f *"Surface water concentrations of SRP and NO_3^--N were monitored in order to compare surface and subsurface water chemistry." …*

P10l28: missing r in break

was corrected

P11l7: Here you mention declining concentrations with depth, but figure 3 shows fluxes. Adding concentrations to figure 3 would also be informative

We did measure flux (J_N) not concentration, so this was just wrong and is corrected now to J_N.
Concentrations are not directly measured with the HPFM, however an estimate for the average concentration can be derived by dividing nutrient flux by Darcy velocity. These estimates are illustrated in Figure 5 (for comparison with MLS)
Also see P13 L31 "*In order to facilitate direct comparison, nutrient fluxes as measured in the HPFMs were converted to flux average concentrations which is the quotient of J_N and the respective q_x"*

P11l13: For this conclusion (52% removal), you need to know that the vertical flux is downward and that groundwater has no impact on the concentration levels. However, the vertical flow is given after this conclusion. Re-order?

We moved the estimates on turnover and removal rates to a separate paragraph at the end of this chapter (see 3.2.2.)

P12l6: Higher should be lower?

Yes, you are right! We apologize!

P12l10: Discussion: You may consider to add a paragraph about the applicability of the HPFM. Can it also be applied to quantify vertical nutrient fluxes in lakes and other non-flowing surface waters? Is it applicable in case of a coarse grained hyporheic zone (stones, gravel)?

In general a different design is needed to assess vertical fluxes. Layton et al (2015) assessed vertical contaminant fluxes in river beds with PFMs. We mention this study in our revised article. P14 L26f "*An earlier study on passive flux meter (SBPFM) in river beds (Layton, 2015) only assessed vertical flow of contaminants and is therefore not comparable to the application presented here.* "
Also we added a line on the problems which might arise from coarse sediments
P16 L1ff "*While the installation of mini-drive points or heat pulse sensors in sediments coarser than sand is difficult or even impossible and also proved unfeasible at our field site, installation of the HPFM with the presented technique was successful. The correction for convergence of flowlines into the device or divergence around it is relatively simple and already incorporated in the equation for the flux calculation. We believe that it is applicable for a wide range of field conditions. However, for very coarse sediments, a protection of the HPFM with a well screen might still be preferred*"

P12l10: Discussion: The difference in concentrations measured in the MLS are quite different from the HPFM (figure 5). Is this only due to the diurnal variations? Other explanations? How do we know which method is the best one?

We added a paragraph, discussing the discrepancies between the two measurements (HPFM and MLS). In general, both measure different things (flux/concentration), so it will depend on the specific research question which is "the best" one.

P16 L10ff "*In June, we found discrepancies between the average concentrations measured in the HPFM and the concentration found using the MLS. From our measurements it is not possible to proof that the HPFM results are correct and the MLS results biased. However, the HPFMs showed the expected decline in JN, whereas in the MLS pore water concentrations were similar at all depths assessed. This can be related to two reasons: First, we sampled surface water which bypassed along the wall of the MLS in June but not in October. Second, we sampled the MLS at a time point, when the hyporheic zone was inactive in respect to nutrient processing. Considering the high diurnal amplitudes in hyporheic oxygen, we assumed that the discrepancy between HPFM and MLS arose from oscillations in hyporheic nutrient concentrations similar to the oxygen pattern."*

P12l14: remove second(Layton , 2015)

was corrected

P12l18 two points at the end

was corrected

P14l15: Is this really permanent removal for PO4? Or can it later be released from its absorption sites?

was corrected to a *removal (uptake or adsorption) rate for SRP*

R. González-Pinzón (Referee)

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Please find my general and specific comments within the attached pdf.

I think this work has enormous potential to open an unexplored window of observation, but the manuscript has to be reorganized to convey a clear take-home message. I think that the main work to be done in the revision process is to define the actual scope of the manuscript, i.e., is this a methods paper with strong focus on the technological development? or is this a data-driven paper which presents novel, previously unattainable measurements (with a new technology) that revolutionize our understanding of biogeochemical processing?

Dear Mr. González-Pinzón,

thank you very much for your comments and corrections! Following the suggestion from you and other reviewers, we reorganized the structure of our article. As also noted by reviewers, the amount of data collected in our study (density of measurements) is not sufficient to make robust (e.g. statistically supportable) statements about the biogeochemical processes at our study site. We therefore decided to clearly focus our article on the evaluation of the methodology. The field study was mainly used to demonstrate the applicability of HPFM and to identify benefits and potential limits of the method. Besides that, we used the results to give an example how HPFM derived data can be interpreted. The revised manuscript clearly tracks that story.

We accounted for corrections of orthography or grammar where indicated by you or by other reviewers.

Please find our responses to your specific comments in the separate commented pdf file.

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Quantifying nutrient fluxes in Hyporheic Zones with a new Passive Flux Meter (HPFM)

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Abstract. The hyporheic zone is a hotspot of biogeochemical turnover and nutrient removal in running waters. However, due to methodological constraints, our quantitative knowledge on nutrient fluxes to those reactive zones is still limited.

In groundwater systems passive flux meters, devices which simultaneously detect water and nutrient flows through a screen well in the subsurface, proofed to be valuable tools for load estimates.

Here we present adaptations to this methodology and a smart deployment procedure which allow its use for investigating water and solute fluxes in river sediments. The new hyporheic passive flux meter (HPFM) delivers time integrating values of horizontal hyporheic nutrient fluxes for periods of several days up to weeks. Especially in highly heterogeneous environments like the hyporheic zone, measuring flow and nutrient concentration in a single device is preferable when compared to methods that derive flux estimates from separate measurements of water flows and chemical compounds.

We constructed HPFMs of 50 cm length, separated in 5-7 segments which allowed for vertical resolution of horizontal nutrient and water transport in the range of 10 cm. The results of a seven day long field test, which included simultaneous measurements of oxygen and temperature profiles and manual sampling of pore water, revealed further advantages of the method: While grab sampling of pore water could not account for the high temporal variability of nitrate fluxes in our study reach, HPFMs accumulatively captured reliable values for the complete deployment time. Mass balances showed that more than 50 % of the nitrate entering the hyporheic zone was removed in the assessed area.

Being low in costs and labor effective, many flux meters can be installed in order to capture larger areas of river beds. The extended application of passive flux meters in hyporheic studies has therefore the potential to deliver the urgently needed quantitative data which is required to feed into realistic models and lead to a better understanding of nutrient cycling in the hyporheic zone.

Keywords: hyporheic exchange, nutrient retention, quantitative methods, running waters, stream metabolism

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1 Introduction

~~Northern and central European~~ rivers export high loads of nitrogen from inland catchments to the marine environment. The ecological and economic problems caused by eutrophication of coastal and riverine ecosystems systems have been recognized years ago (Artioli et al., 2008;Skogen et al., 2014;Patsch and Radach, 1997). Decades of nutrient studies have unveiled, that rivers cycle rather than only transport nutrients (Seitzinger et al., 2002;Galloway et al., 2003;Garcia-Ruiz et al., 1998a). However, the quantitative dimensions of instream dynamics of nitrogen (N) and other nutrients are still not completely understood (Wollheim et al., 2008;Grant et al., 2014). Even though dissimilatory nitrate reduction to ammonium (DNRA) and subsequent anaerobic ammonium oxidation (anammox) might be of importance in some systems (Smith et al., 2015), in most river systems, nitrate (NO_3^-) removal via denitrification, the anaerobic reduction of NO_3^- to gaseous N_2 is the dominant dissimilatory process which removes N out of the system (Laursen and Seitzinger, 2002;Bernot and Dodds, 2005;Lansdown et al., 2012). Various studies found that in-stream denitrification exclusively happens at "reactive sites" in the hyporheic zone (Duff and Triska, 1990;Rode et al., 2015). The hyporheic zone is defined as the subsurface region of streams and rivers that exchanges water, solutes and particles with the surface (Valett et al., 1993). The occurrence of anaerobic areas, the buffering of variations in flow, temperature or water chemistry, a continuous supply with nitrate and carbon provide a benign habitat for denitrifying microbes (Garcia-Ruiz et al., 1998b;Opdyke et al., 2006;Alexander et al., 2009;Zarnetske et al., 2011a). As a result of much higher residence times hyporheic transient storage was recognized to have a stronger influence on overall removal of NO_3^- and other nutrients like phosphate (P) when compared to surface water storage zones (Basu et al., 2011;Stewart et al., 2011). However, even in nitrogen saturated systems like agriculturally impacted groundwater and streams, denitrification can be limited by NO_3^- availability, because consumption in the hyporheic zone is faster than resupply of solutes (Fischer et al., 2009;Böhlke et al., 2009;O'Connor and Hondzo, 2008;Harvey et al., 2013).

In addition to remove nutrient loadings at larger time scales (e. g. seasonal or annual), intermediate storage disperses the propagation of pollutant spikes which could be harmful for receiving water bodies (Findlay et al., 2011). In stagnant waters, such as lakes, the transport of dissolved nutrients to the sediments is dominantly controlled by diffusion. Therefore, surface water concentrations of nutrients are a good predictor for uptake processes and potential limitations (Dillon and Rigler, 1974;Jones and Bachmann, 1976). In rivers, hydrological processing and physical storage of nutrients were found to be as important or ~~of~~ even ~~higher importance than~~ biological uptake capacity (Covino et al., 2010;Runkel, 2007;Brookshire et al., 2009), because the transport of solutes to reactive sites is determined by advection rather than diffusion (Grant et al., 2014;Wörman et al., 2002). As a result, it is not possible to interpret hyporheic processing rates from surface water observations, if subsurface fluxes and transport velocities are unknown. ~~Nutrient flux (i.e. the product of nutrient concentration and specific discharge) is conclusively a much better metric for hyporheic turnover rates than concentration alone.~~

Several numerical or empirical models demonstrated the complexity of surface – subsurface exchange of water and solutes. Exchange rates could be attributed to surface flow, water level, sediment properties and various other hydrological, chemical and physical factors (Trauth et al., 2015;Boano et al., 2014;Böhlke et al., 2009).

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While NO_3^- has been the main focus of hyporheic nutrient studies, in-stream P cycling has recently received increasing interest (Boano et al., 2014;Mulholland et al., 2009). Even though the earliest studies of hyporheic nutrient dynamics focused on P (Mulholland and Webster, 2010;Hall et al., 2009), only very few studies have attempted to directly assess P transport in the hyporheic zone (Boano et al., 2014). Based on the fact that the mobility, transformation and retention of phosphate (PO_4^-) are mainly dependent on redox conditions which are directly coupled with NO_3^- concentrations (Smith et al., 2011;McDaniel et al., 2009;Gabriel et al., 2006) hyporheic transport studies should address NO_3^- and phosphate fluxes simultaneously.

Small changes in [illegible]m state or water chemistry ~~variables~~ were found to significantly alter hyporheic zone nutrient processing. Hence quantitative models are fraught with high uncertainties while experimental investigations of nitrate turnover rates in the hyporheic zone are often exclusively of qualitative nature (Grant et al., 2014;Mulholland [illegible], 1997). As a result, for both, N and P, there is urgent need ~~for quantitative measurements of~~ nutrient flux through the hyporheic zone~~: On one hand,~~ to support ~~the modelled results~~ (Alexander et al., 2009; [illegible]er et al., 2006;Wagenschein and Rode, 2008), ~~on the other hand,~~ to ~~provide a solid basis for the discussion on~~ the ~~importance~~ of hyporheic processes in whole stream NO_3^- uptake (Fischer et al., 2009). While the importance of subsurface [illegible]ways for N-cycling is widely acknowledged (Seitzinger et al., 2006;Zarnetske et al., 2012), there is still disagreement on the amounts of nutrient loadings actually reaching the reactive sites in the subsurface (Fischer et al., 2005;Zarnetske et al., 2011b).

Whilst understanding of ~~surface water~~ NO_3^- cycling has ~~remarkably~~ improved in ~~the~~ recent years, benefiting from newly emerging sensors ~~which~~ deliver high resolution time series of nutrient concentrations (Pellerin et al., 2009;Hensley et al., 2014;Rode et al., 2016), ~~equivalent~~ technics ~~are not available for subsurface studies.~~ ~~Here~~ tracer injections and ~~/or manual~~ sampling are ~~still~~ the only approach for ~~observing~~ th[illegible] of NO_3^- and other nutrients (Fischer et al., 2009;I[illegible]dahl et al., 2009;USEP, 2013).

Nutrient uptake measurements based on whole stream tracer injections and mass balances (Böhlke et al., 2009;McKnight et al., 2004) have been used for determining general uptake dynamics on the reach scale, but did not identify the reaction site (hyporheic versus in channel or algal canopies) or specific local uptake processes (Ensign and Doyle, 2006;Ruehl et al., 2007). More important, in-stream measurements do exclusively account for water which is re-infiltrating into the main stem after passage through the hyporheic zone. Under loosing conditions, where most of the surface water nutrient-influx is flowing towards the groundwater, processing rates in the hyporheic zone cannot be observed in the surface water. Likewise, if groundwater is contributing significantly to surface water chemistry, surface water mass balances do not characterize nutrient cycling in the hyporheic zone realistically (Trauth et al., 2014).

Other attempts are based on benthic chamber and incubation experiments (Kessler et al., 2012;Findlay et al., 2011). Those laborato[illegible] mesocosm and flume experiments ~~deliver~~ rates of denitrification potential of the substrates, usually ~~assessed~~ via denitrification enzyme assays (DEA). N[illegible]heless, it ~~was~~ found that ~~the realized~~ denitrification rate ~~is~~ determined by environmental and hydrological conditions rather than by substrate type or denitrification potential (Findlay et al., 2011). Likewise ~~would~~ small scale fluctuations in hyporheic flow and metabolic activity influence the redox conditions and thereby the binding and mobilization of phosphorous. Due to those natural

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variations and the complexity of environmental conditions, hyporheic transport of nutrients cannot satisfactorily be mimicked in artificial ~~set ups~~ (Cook et al., 2006~~). Hence, those attempts neglect many important hydrological, biophysical and chemical processes that influence the nutrient fate and transport~~ (Grant et al., 2014).

Separately measuring exchange rates via hydraulic head differences or tracer injections and pore water nutrient concentrations have often been the methods of choice (Saenger and Zanke, 2009;Alexander et al., 2009). These methods provide valuable insights into the time specific conditions at the target site. However, hyporheic zone processes are highly variable in time and space (Cooke and White, 1987), which can lead to high uncertainties if separated measurements are used to characterize a single parameter (e. g. nutrient flux). Additionally, attempting to characterize larger areas with these methods or account for short term variability is laborious and costly. ~~However, as long as~~ grab sampling is not repeated at high frequencies it ~~can~~ exclusively ~~be interpreted as a~~ snap shot ~~which do~~es not allow a characterization of the system. Conclusively, long term measurements are required to obtain ~~an~~ integrative mass flux signal.

Measuring solute fluxes through porous media ~~is also aspired~~ in groundwater studies. There, passive flux meters (PFM) have successfully been used to quantify fluxes of dissolved nutrients (Cho et al., 2007) and contaminants (Annable et al., 2005;Verreydt et al., 2013;Hatfield et al., 2004) through screened groundwater monitoring wells. PFMs allow determination of the horizontal water flux through the screened media from the dilution of a resident tracer and to simultaneously capture the amount of transported target solute (nutrient or contaminant) using a permeable sorbent. Observation time can range from days to weeks~~, so that the time averaged solute flux during that defined period can be monitored.~~ A method for quantifying vertical mass flux through sediments (SBPFM) has recently been developed and field testing has been initiated (Layton, 2015)

~~T~~he application of PFMs in hyporheic zones, several adaptations are necessary. Most importantly, the flow velocities and the masses of transported solutes are expected to be several orders of magnitude higher in hyporheic zones than in the groundwater. Thus, a suitable sorbent for the target nutrients with ~~appropriately~~ high loading capacity is required. The market of anion absorbing resins, originally manufactured for water purification purposes, is huge and offers a wide range of products with varying characteristics (Annable et al., 2005;Clark et al., 2005). Various criteria, like possible interference of resin compounds with the resident tracer analysis or the hydraulic conductivity of the resin have to be considered depending on the study site and research question.

Additionally, a new deployment and retrieval procedure has to be developed, because contamination with surface water has to be avoided. In hyporheic studies the flux meter should be in direct contact with the surrounding sediments with a minimal manipulation of the natural flow pattern.

~~F~~hermore, PFMs have so far been used in waterbodies which were not subjected to light or high temperatures and where nutrient concentrations were low. Hence, biofouling on the meters was not regarded in previous studies.

In this study we present the modification of the passive flux meter for applications in the hyporheic zone (Hyporheic Passive Flux Meter, HPFM) with the example of N and P in a nutrient rich 3rd order stream (Holtemme, Germany) with a strong anthropogenic impact gradient (Kamjunke et al., 2013)

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2 Methods

2.1. Construction and materials

The Hyporheic Passive Flux Meters (HPFM) consisted of a nylon sock which was filled with a mixture of a macroporous anion exchange resin as a nutrient absorber and a tr[illegible]oaded carrier. In the present study we constructed them in a 50 cm long, 5 cm Ø cylindrical form. A stainless steel rod in the middle assured the stability of the device (**Figure 1**).

To detect vertical gradients of both nutrient and water fluxes in the hyporheic zone, the HPFM was divided into several segments by rubber washers. Steel tube clamps were used to attach the nylon sock to the steel rod placed in the center of the HPFM. The nylon mesh for the socks was purchased from Hydro-Bios (Hydro-Bios Apparatebau GmbH, Kiel-Holtenau, Germany) and is available in a wide range of mesh size and thicknesses. We used a mesh size of 0.3 mm. A rope was connected to the tube clamp on the upper end of the HPFM in order to facilitate retrieva

2.1.1. Preparation of activated carbon

Similar to the groundwater PFM, silver impregnated activated carbon (AC) was used as sorbent for the resident trace[illegible]e AC used for the HPFM in this study was provided by the University of Florida, Gainesville and was prepared as reported (Annable et al. 2005). By choosing the same manufacture as used in the above mentioned studies, we could rely on physical and chemical characterization and calculated retardation factors for alcohol tracer partitioning behavior which have been established by Hatfield et al. (2004) and Annable et al. (2005).
The magnitude of water flow through the flux meter is unknown in the field applications, therefore multiple resident tracers with a wide range of tracer elution rates were used (Hatfield et al., 2004;Cho et al., 2007). An alcohol tracer mixture for approximately 10 HPFM was prepared by combining 100 mL of methanol, 100 mL of ethanol, 200 mL of isopropanol (IPA), 200 mL of tert-butanol (TBA) and 66 mL of 2, 4-dimethyl-3-pentanol (2,4 DMP) (Cho et al., 2007).
[illegible]n aqueous solution of resident alcohol tracers, a standard ratio of 13 mL tracer mixture was transferred to 1 L water in a Teflon sealed container and was then shaken by an automated shaker over a period of several hours. Subsequently, 1.5 L of dry activated carbon was added to the aqueous tracer solution and rotated for 12 hours to homogenize the AC tracer mixture. Following mixing, the AC tracer mixture was stored in a sealed container and refrigerate

2.1.2. Deployment and retrieval procedure

HPFMs were built, stored and transported in 70 cm long standard polyethylene (PET) tubes (58 x 5.3 SDR 11) purchased from a local hardware store (Handelshof Bitterfeld GmbH, Bitterfeld, Germany). To avoid resident

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alcohol tracer loss, the transport tubes with the HPFMs were sealed with rubber caps and cooled during storage and transport.

On site, prior to ~~installing~~, the HPFMs were transferred to a stainless steel tube (5.3 cm inner diameter) with a loose steel drive point tip on the lower end. The steel casing and HPFM were driven into the river bed using a 2 kg hammer until the upper end of the HPFM was at the same level as the surface-subsurface interface. The metal casing was retrieved while the HPFM was held in place using a steel rod.

After a specific period of exposure, the HPFM was retrieved by holding the transport tube in place and quickly drawing the HPFM into the tube using the rope fixed to the upper end of the HPFM. The required length of the transport tube, steel drive casing and retrieval rope was determined by the depth of the water level in the stream.

After retrieval, the HPFMs were transported to the laboratory, where they were removed from the transport tube for sampling. Each segment was cut open and the sorbent mixture was recovered, homogenized and a subsample transferred to 40 mL glass via

2.2. Analysis and data treatment

2.2.1. Water flux

The AC samples were shipped to the University of Florida for analysis. In the laboratory, the tracer mass in standard AC samples and the tracer mass remaining in the final AC samples were extracted ~~by~~ iso-butyl alcohol (IBA). About 10 g of AC samples were collected into pre-weighed 40 mL vials containing 20 mL IBA. Vials were rotated on a Glas-Col Rotator, set at 20 % rotation speed, for 24 h. Then, subsamples were collected in 2 mL GC vials for alcohol tracer analysis. The samples were analyzed ~~by~~ a GC-FID (Perkin Elmer Autosystem) (Cho et al. (2007).

The relationship between time average specific discharge through the device and tracer elution is given by ~~the~~ equation (1) (Hatfield et al., 2004)

$$q = \frac{1.67\, r\theta\, (1-M_R)\, R_d}{t} \quad (1)$$

where r (m) is the radius of the HPFM, θ is the water content in the HPFM ($m^3\ m^{-3}$), M_R is the relative mass of tracer remaining in the HPFM sorbent, t is the sampling duration and R_d is the retardation factor of the resident tracer on the sorbent.

The retardation factor R_d ~~is a measure for~~ the rate of elution of a particular alcohol from the AC. R_d for the specific set of tracers and AC used in this study had previously been determined by the relationship between tracer mass loss and the cumulative water flow by Hatfield et al. (2004) and Annable et al. (2005) (**table 1**).

2.2.2. Nutrient flux

All values for NO_3^- and PO_4^- in this article are noted as NO_3^--N or PO_4^--P respectively if not indicated otherwise.

NO_3^- and PO_4^- were extracted and analyzed in the laboratory at UFZ in Magdeburg, Germany.

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For extraction, 30 mL of 2M KCl was added to 5 g of resin and rotated for 24hours. The solution was then analyzed on a Segmented Flow Analyser Photometer (DR 5000, Hach Lange): NO_3^--N at 540 nm (precision of 0.042 mg L^{-1}), SRP at 880nm (precision 0.003 mg L^{-1}).

The time-averaged advective horizontal nutrient flux can be calculated by the following relationship (Hatfield et al., 2004):

$$J_N = \frac{qM_N}{2\alpha rLt} \quad (2)$$

Where M_N (kg) is the mass of nutrient adsorbed, L (m) is the length of the vertical thickness of the segment, α (-) is a factor that characterizes the convergence or divergence of flow around the HPFM.

Laboratory experiments

Experiments described in this paragraph were accomplished on triplicate samples, if not indicated otherwise. A nutrient sorbent had to meet the following criteria:

a) Have a high loading capacity for NO_3^-, PO_4^- and competing anions

b) Be free of compounds which could interfere with the alcohol tracer measurements (e.g. organic substances)

c) Have a low background of NO_3^- and PO_4^-

A pre-selection for anion-absorbing resins which were free of organic compounds was made based on information provided by the manufacturers (Purolite®, Lewatit®, Dowex®). Nutrient background was then determined by extracting and analyzing NO_3^- and PO_4^- from 5 g of each pure resin as described above. Extractable background concentrations were then converted to nutrient fluxes using a Darcy flux of 45 mm h^{-1}, an estimate of hyporheic flow velocity based on prior salt tracer tests at the study side. Likewise expected hyporheic nutrient flux was computed from previously examined concentrations in pore water samples and above-mentioned hyporheic flow. The only resin with nutrient background below 5 % of expected concentrations was Purolite® A500 MB Plus (Purolite GmbH, Ratingen, Germany), which had extractable background NO_3^- of 8 µg NO_3^--N g^{-1} wetted resin and 0.08 µg PO_4^--P g^{-1} resin. Purolite® A500 MB Plus was then considered for further testing.

For the determination of the loading capacity, three 5 cm diameter columns were filled to a height of 5 cm with wetted Purolite® A500 MB Plus resin and infiltrated with water collected from the study reach. The columns were covered with tin foil to keep out light and ensure stable temperature. A constant supernatant of 1 cm was kept on all three columns. Water was continuously pumped through the columns at a speed of 20 mL h^{-1}, which also equals the expected Darcy velocity of 45 mm h^{-1}. The draining water was sampled twice a day and analyzed for SRP and NO_3^-. Biofilm growth on the resin was assessed by repeating the same experiment in smaller columns and extending it for several days after break-through occurred. That way, nutrient consumption by biofilm after the exhaustion of the loading capacity could be monitored. Additionally, samples of resin granules were colored with SybrGreen ($C_{32}H_{37}N_4S^+$) on nucleic acid and examined under a confocal laser scanning microscope, to depict the degree of bacterial fouling on the granular surface.

Concurrent to the resin, AC was tested for background nutrients by extraction with 30 ml KCL per 5 g AC.

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The activated carbon contained 0.01 mg PO_4^--P g^{-1}AC and 0.08 mg NO_3^--N g^{-1} AC, which amounts up to 75 % of expected concentration for nitrate and 320 % for SRP. To investigate whether the AC could be cleaned by washing, we repeatedly treated AC samples with distillated water or KCl as depicted in the extraction description above. Nutrients did not leach ~~of~~ under water treatment and neither did KCl treatment satisfactorily reduce extractable background concentration on the AC. After the third washing of AC with KCl, ~~still~~ 0.02 mg PO_4^--P and 0.04 mg NO_3^--N could be extracted per g AC. Further, it is unclear to which degree replacing absorbed nutrients by KCl would alter the alcohol tracer retardation and extraction on the AC. For those reasons ~~it was~~ decided to keep the nutrient absorbing resin separated from the AC. As AC did not release background nutrients water flowing through AC and afterwards resin layers ~~was~~ not considered problematic.

2.4. Field testing of hyporheic passive flux meters (HPFMs)

2.4.1. Study site

A 30 m long stretch of the Holtemme River, a 3rd order stream in the Bode catchment, TERENO Harz/Central German Lowland Observatory, served as study site (51°56'30.1"N, 11°09'31.8"E) (**figure 3**). The testing reach is located in the lowest part of the river, where the water chemistry is highly impacted by urban effluent and agriculture (Kamjunke et al., 2013). Long stretches have been subjected to changes in the natural river morphology by canalization (Sachsen-Anhalt Landesbetrieb für Hochwasserschutz und Wasserwirtschaft, 2009).

The sediment at the selected site ~~is~~ mainly sandy ~~with~~ gravel and stones ~~mixing in~~. Clay lenses are present in the deeper sediments below 35 cm.

Mean discharge is 1.35 m^3 s^{-1} with highest peaks around 5-6 m^3 s^{-1}. Discharge is continuously recorded by the local authorities at the gauge Mahndorf, 15 km upstream of the testing site. In the course of the year, NO_3^--N concentrations in the lower Holtemme vary between 2 and 8 mg NO_3^--N L^{-1}(LHW, 2015/2016).

2.4.2. HPFM testing

The equipment was installed for a period of 7 days from 4th to 11th June 2015 as illustrated in **figure 2**.

Based on the laboratory results for the nutrient backgrounds, two approaches for constructing and deploying HPFMs were ~~field~~ tested.

A) Resin only and AC only HPFMs

4 HPFMs were constructed of which 2 contained only resin (R1 and R2) and the other two contained only AC (AC3 and AC4). The HPFMs were then installed in pairs: AC only and resin only next to each other with a separation distance of 30 cm. Those 4 HPFMs were sectioned in 5 horizontal flow segments, each with a vertical length of 10 cm.

For the calculation of the nutrient flux through each segment of R1 and R2, we used the corresponding water flux through the respective segment of AC3 and AC4.

B) Alternating segments of AC and resin HPFMs

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HPFMs L5 and L6 consisted of 7 segments starting and ending with an AC segment and interjacent segments altering between resin and AC (also see **figure 1**). Each segment had a length of 7 cm.

For the calculation of the nutrient flux through the resin segments we used the interpolated water flow measured in the two adjacent AC segments.

A control HPFM equal to the HPFMs with alternating segments was stored and transported together with the other HPFMs. After deploying the control HPFM, it was immediately retrieved, transported back to the laboratory and stored until it was sampled and analyzed along with the other HPFM

2.4.3. Additional measurements

Vertical Darcy velocity (q_v)

The vertical Darcy velocity (q_v) (m d^{-1}) in the streambed was calculated using temperature profiles measured between January 2015 and October 2015. According to Schmidt et al. (2014) vertical flow velocities can be computed from the temporal shift of the daily temperature signal in the subsurface water relative to the surface water. A multi-level temperature sensor (Umwelt und Ingenieurtechnik GmbH, Dresden, Germany) was installed at the test site in January 2015. Temperature was recorded at the surface-subsurface interface and at depths of 0.10, 0.125, 0.15, 0.2, 0.3 and 0.5 m in the sediment at a 10 min interval (accuracy of 0.07 °C over a range from 5 to 45 °C, and a resolution of 0.04 °C)

Oxygen profiles

Two oxygen loggers (miniDO$_2$T, Precision measurement engineering Inc.) were installed in the river bed at depths of 25 and 45 cm below surface-subsurface boundary. Installation was carried out 4 weeks prior to the experiments, allowing enough time for re-equilibration of the surrounding media. The measurement time step was 5 min.

Multi-level samplers (MLS)

Multi-level samplers as described by (Saenger and Zanke (2009)) are devices for the manual extraction of hyporheic pore water from several distinct depths. The two samplers A and C used in these experiments were manufactured by the institutional workshop of the UFZ. They consisted of an outer stainless steel tube with a length of 50 cm and a diameter of 5 cm. Ceramic filters were inserted in this outer steel mantle marking the extraction depths at 5, 15, 25 and 45 cm. The inner sides of the filters were attached to steel pipes that ran to the top of the sampler so that Teflon tubes could be attached. A protective hood was threaded on the upper end of the sampler to preclude particles and sediment entrance. Pore-water was manually extracted by connecting syringes to the open end of the Teflon tubes and slowly sucking up wate

A sample volume of about 10 mL was filtered in the field and placed in glass vials for transport to the laboratory. Analysis for NO_3^-, SRP, sulphate (SO_4^{2-}) and Boron (B) were conducted in the analytical department of the UFZ. Analytical procedure for NO_3^- and SRP was according to the description above.

SO_4^{2-} and B were used as natural tracers for groundwater and surface water respectively. SO_4^{2-} was analyzed on an ion chromatograph (ICS 3000, ThermoFisher, former DIONEX), B was analyzed on an inductively coupled plasma mass spectrometer (ICP-MS 7500c, Agilent)

Manual pore-water samples were taken twice during the installation period of the HPFM: on the 4th and 11th of June 2015, both times between 1 pm and 4 pm local time.

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to conflicting findings in the pore water samples taken on June 4th and 11th 2015, the sampling was repeated on the 8th of October. In October, each device was sampled twice, the first time in the early morning before sun rise and again in the early afternoon (around 2 p

Surface water chemistry was monitored with two sets of sensors: upstream and downstream of the reach. For this we installed automated UV absorption sensors for NO_3^- (ProPS WW, TriOS) on the beginning of the testing reach and 1.5 km downstream for the duration of the experiments. The pathway-length of the optical sensor was 10 mm, measuring at wavelengths 190-360 nm with a precision of 0.03mg NO_3^--N L^{-1} and an accuracy of ± 2 %. The measurement time step was set to 15 min.

Both UV sensors were supplemented with a multi-parameter probe YSI 6600 V2/4 (YSI Environmental, Yellow Springs, Ohio) recording the following parameters: pH (precision 0.01 units, accuracy ± 0.2 units), specific conductivity (precision 0.001mS cm^{-1}, accuracy ± 0.5 %), dissolved oxygen (precision 0.01 mg L^{-1}, accuracy ± 1%), temperature (precision 0.01 °C, accuracy ±0.15 °C), turbidity (precision 0.1 NTU, accuracy ± 2 %) and chlorophyll-a (precision 0.1 µg L^{-1}, linearity: R^2>0.9999 relative to dilution of Rhodamin WT solution of 0 to 400 µg L^{-1}).

2.4.4. Nitrate transport and denitrification

Flux and denitrification activity for the specific conditions at the study site during the HPFM testing phase were calculated using the morphological and hydrological parameters summarized in **table 2.**

The proportion of water infiltrating the hyporheic zone was then calculated as the ratio $\frac{Q_{HZ}}{Q_{SW}}$. Where Q_{HZ} (m^3 s^{-1}) is the product of the average horizontal Darcy velocity q_x (m s^{-1}) measured in the HPFM and the cross sectional area of the upper 50 cm of the hyporheic zone A_{HZ} (m^2).

NO_3^- removal activity of the hyporheic zone (%) was calculated from the difference in surface water concentration $C_{NO3\text{-}SW}$ and the average concentration observed in the HPFM ($C_{NO3\text{-}HZ}$).

3. Results

3.1. Laboratory experiments

3.1.1. Loading capacity

Break-through in the sorbent column experiments occurred after 300 pore volumes (PVs) or 21 days at selected drainage for both NO_3^- and SRP. The minimal absorbing capacity as calculated from parameters indicated in the product sheets of Purolite® A500 MB Plus was 265 PVs, equaling 19 days in the described set up.

In the biofouling experiment, the NO_3^- concentration in the draining water gradually decreased again after beak-through. SRP in the draining water was completely depleted 6 h after the break-through. We attributed the decrease of nutrients in the draining solution after breakthrough to biotic consumption of SRP (limiting nutrient) and NO^{3-} .

Under the laser scanning microscope growth of biofilm could be observed on all of the examined Purolite® beads.

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3.2. Field testing

Deployment required approximately 15 min per HPFM and could be conducted by two persons. The water depth during the installation was 40 to 100 cm, depending on the specific location in the stream. The results from the control HPFM proved that tracer loss or nutrient accumulation during transport, deployment and retrieval was negligible.

The average horizontal water flow q_x and nutrient flux measured in the HPFM during the 7 day field testing are illustrated in **figure 3**. All flux meter, except ~~5L1~~ showed declining concentrations and q_x with depth. Average horizontal q_x was 76 cm d^{-1}, ranging from 115 cm d^{-1} in the shallowest layer of ~~5L1~~ to 20 cm d^{-1} in the deepest layer of AC4)

With an average water flux of Q_{HZ} = 2.65 e^{-5} m^3 s^{-1} through the assessed upper 50 cm of the hyporheic zone and across the 6 m width of the stream, 0.008 % of water transported in the river entered the hyporheic zone (**table 3**). While the average surface water concentration was 2.86 mg NO_3^--N L^{-1}, the average concentration in the subsurface measured with the HPFMs was only 1.39 mg NO_3^--N L^{-1}. Accordingly, 52 % of the infiltrating NO_3^- was removed in the hyporheic zone. For SRP the average surface water concentration from 4th to 11th June 2015 was 0.165 mg PO_4^{3-}P L^{-1}, the average concentration in the hyporheic zone was 0.11 mg PO_4^{3-}-P L^{-1}.

Temperature profile

Vertical water flow q_y in the stream bed was predominantly downward from January to October 2015. It was continuously downward during the HPFM testing phase, ranging from 40 to 55 cm d^{-1}. The relation between q_y and q_x ($\tan\alpha = \frac{q_y}{q_x}$) results in an approximate angle of hyporheic flow of 32° downwards, assuming that q_x is directed downstream.

Oxygen profiles

We observed strong diel variations in oxygen concentration in the hyporheic zone. During several nights oxygen was nearly depleted (**figure 4**).The minima and maxima oxygen concentration in the subsurface occurred contemporarily with the respective extremes in the surface wa

Multi-level samplers

The results from the manual pore-water sampling conducted in June 2015 are illustrated in **re 5.** In order to facilitate direct comparison, nutrient fluxes as measured in the HPFM were converted to flux average concentrations using the measured q_x.

In general, nutrient concentrations in the manually sampled pore-water were higher than the average concentration derived from the HPFM. The expected increase of SRP and decrease of NO_3^- and water flow with depths was observed in the HPFM, whereas pore water extracted with the MLS showed no change over depth for neither of the two substances.

Observations during installation and retrieval of the HPFM suggest that HPFM L6 and R4 hit a clay lens in the lowest segments (deeper that 35 cm in the subsurface).

On both sampling dates (04.06. and 11.06.2015) neither SO_4^{2-} nor B showed a vertical gradient in concentrations in the pore water samples. SO_4^{2-} concentrations of 170 mg L^{-1} on the 4th June and 190 mg L^{-1} on the 11th June were in

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the same range than surface water concentrations. Likewise were B concentrations with 50 to 60µg L^{-1} in consistence with the concentrations in the surface water. Conclusively, manually sampled hyporheic zone water was originating exclusively from the surface w

The repeated manual pore-water sampling in October (**figure 6**) showed clear differences in SRP and NO_3^- concentration between early morning and afternoon.

NO_3^- concentrations in the subsurface were in general higher in the early morning hours than in the afternoon. SRP shows the opposite trend: higher concentrations in the early morning.

Surface water NO_3^- concentrations on the sampling day were 2.5 mg NO_3^--N L^{-1} in the morning and 2.7 mg NO_3^--N L^{-1} in the afternoon. SRP concentrations were consistently 0.15 mg L^{-1}.

4. Discussion

The application of the HPFM proved as an innovative tool for the quantitative in situ measurement of NO_3^- and SRP fluxes through the hyporheic zone. Earlier applications of passive flux meter (SBPFM) in river bed studies (Layton, 2015) exclusively assessed vertical flow, so that this is the first study which used HPFM for the quantification of horizontal nutrient transport in the hyporheic zone. (Layton, 2015)In the current work adaptations were developed, tested and improved. Those include the choice of an appropriate resin, assessment of biofilm growth on the instruments and a practice that avoids contamination of the absorber with sorbent inherited nutrients. While both of the latter mentioned practices examined in this study delivered reliable results, each inherits designated characteristics being more or less beneficial for different specifications. .

1) Deploying two HPFMs of which one is used to assess the water flux and the second to capture nutrients. This approach is preferable if a high resolution depth profile is needed (a heterogeneous flux distribution in the vertical direction). Since this approach assumes that local horizontal heterogeneity is negligible in the range of 20-30 cm, we recommend this type for the use in uniform systems such as channelized river reaches.

2) Alternating nutrient absorbing and water flux measuring segments is a good choice if local lateral flux heterogeneity is expected to be high and/or if the vertical profile is moderately heterogeneous.

Further improvements of the HPFM for nutrient studies in the subsurface of rivers could be achieved by identifying a nutrient free carrier for the tracers. First, because this would allow measuring nutrient and water flux at the same location within the device and thereby increase spatial resolution. Second because in a mixed texture of nutrient absorber and tracer carrier the antibacterial nature of the activated carbon would suppress biofouling on the sorbent. Here we showed that substantial biofilm growth occurred on the resin in the laboratory as well as under field conditions. Even though the observations on the column experiments suggest that biofilm growth on the resin porous media did not affect its loading capacity, it is unclear, to what extent the biofilm bound nutrients can be captured by the implemented extraction procedure. As a result, it is not possible to completely exclude that biofouling might lead to underestimation of actual nutrient flux through the HPFMs.

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In addition to instrumental adaptations we presented an installation practice, which allows for smooth deployment with minimal disturbance of the system. Unlike typical well screen deployments where PFMs (Verreydt et al., 2013;Annable et al., 2005) or SBPFM (Layton, 2015) have been inserted into a screened plastic or steel casing, our technique enabled the direct contact of the HPFMs with the surrounding river sediments. Compared to other intrusive measurements of hyporheic flow, the disturbance created by a HPFM is low, because the measuring time is long relative to the duration of the installation. By removing the solid casing, we further improved the integration of the instrument in the natural system and avoid the generation of artificial flow paths along the walls of the device. For very coarse sediments, a protection of the HPFM with a screened plastic or steel casing might still be preferential. A mayor gain of the HPFM method is highlighted by the findings of the 7 day long field testing: Concurrent manual sampling of pore-water from MLSs showed diurnal variations of SRP and NO_3^- in the subsurface of the testing reach. Whereas, as in the first MLS assessment in June 2015 only a single time specific snap shot sampling was conducted, the results may not realistically represent the overall conditions at the target site. Diurnal cycles in benthic metabolism cause temporal variations in various water quality parameters, including many nutrients. As the majority of sampling is commonly conducted during daylight hours, night time conditions are misrepresented in studies relying on single manual sampling events. That flux average concentrations can derivate by more than 50 % from estimates based on single event sampling was illustrated by comparison between our manual samples and the average pore-water concentrations calculated from the HPFM data.

We consider that a combination of pore water samples for diurnal dynamics and long term recording of nutrient transport through the hyporheic zone via HPFM is a valuable approach that can be efficiently used to characterize and quantify nutrient dynamics in a sediment system. Presumably, for our field test, the lower NO_3^- concentrations in the subsurface in the early morning hours compared to afternoon samples detected in the MLS samples in October can be attributed to a dominance of night time denitrification. DO exhibited strong diurnal cycles with anoxic periods occurring in the subsurface during night times periods. This temporal pattern, owing to microbial consumption of O_2 in the sediment, is commonly found in nutrient rich streams (Nimick et al., 2011;Harrison et al., 2005) and identified as triggering factor for night time denitrification in the hyporheic zone (O'Connor and Hondzo, 2008;Laursen and Seitzinger, 2004;Christensen et al., 1990). Presumably, the redox conditions in the subsurface also regulated the mobilization/demobilization of phosphate (Smith et al., 2011). Reducing conditions during night periods enhanced the mobilization of PO_4^-. During day elevated O_2 and NO_3^- concentrations suppressed the reduction of Fe^{3+} (Miao et al., 2006), PO_4^- was therefore demobilized and SRP was decreasing (Gabriel et al., 2006). Accordingly, SRP concentration in hyporheic pore water samples was higher in the early morning than in the afternoon. Concurrent measurements of pore water oxygen concentrations as presented in this study are therefore essential to interpret nutrient dynamics. To our knowledge there is a lack of studies which examine the diurnal pattern of nutrients in the hyporheic zone and no studies which actually measured th

Like solute concentrations and water flow patterns, the vertical extension of the hyporheic zone varies in time and space and between different rivers and reaches. Our set up assessed exclusively the upper 50cm of the hyporheic zone. We found that this entire area (and potentially deeper) of the subsurface contained active sites for denitrification. While some studies have found that denitrification is limited to the upper few cm of the hyporheic

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zone close to the sediment-water interface (Hill et al., 1998;Harvey et al., 2013), our results are in accordance to findings by Zarnetske et al. (2011b) and Kessler et al. (2012) who also report extended active hyporheic zones. As vertical water movement was constantly downward and the lowest concentrations of NO_3^- were observed in the deepest segments of the HPFMs, the hyporheic zone at this study site likely extends deeper than the 50 cm evaluated. The length of an HPFM can easily be increased, depending on the individual site conditions.

The hyporheic removal potential of more than 50 % of infiltrating NO_3^- and 30 % of SRP is clearly an indication of an active hyporheus. Evaluation of the effect of hyporheic denitrification activity on overall nitrate removal in the stream or the normalization of hyporheic uptake to a benthic area requires the length of the hyporheic flow path, which can be derived from the residence time of water and solutes in the hyporheic zone τ_{HZ} and the Darcy velocity q_x. Assuming a downward flow direction, τ_{HZ} could be inferred from the vertical Darcy velocity q_y as assessed from the temperature profiling and the hyporheic zone depths of 50 cm. Thereafter, τ_{HZ} conceptually corresponds to the time the water travels through the hyporheic zone before exiting to groundwater and s_{HZ} to the horizontal vector of the flow paths. The denitrification rate $U_{NO3\text{-}HZ}$ (mg NO_3^--N m^{-2} d^{-1}) is then the difference between the theoretically transported NO_3^- mass $M_{NO3\text{-}HZ\ theor}$, which is the product of Q_{HZ} and $C_{NO3\text{-}SW}$ and the measured mass flux $M_{NO3\text{-}HZ\ real}$. During the testing phase $U_{NO3\text{-}HZ}$ was calculated as 693 mg NO_3^--N m^{-2} d^{-1}. The same procedure yields a removal rate for SRP of $U_{PO4\text{-}HZ}$ = 24 mg PO_4^--P m^{-2} d^{-1}.

5. Conclusion and Outlook

The role of the hyporheic zone as a hot spot for instream nutrient cycling is indisputable (Mulholland et al., 1997;Fellows et al., 2001;Fischer et al., 2005;Rode et al., 2015). The loss of this essential function may be crucial under anthropogenic forcing, such as morphological alteration (Borchardt and Pusch, 2009), eutrophication (Ingendahl et al., 2009)and sediment loading (Hartwig and Borchardt, 2015). In all these cases, mass transfer to the hyporheic zone may be the rate limiting step for nutrient removal (Basu et al., 2011).

Despite decades of research on hyporheic nutrient cycling, robust quantitative data on horizontal nutrient fluxes through the hyporheic zone are limited, which is mainly due to methodological constraints in measuring nutrient concentrations and water flux in the subsurface of streams (O'Connor et al., 2010;Boano et al., 2014;Gonzalez-Pinzon et al., 2015).

Passive flux meters have the potential to fill the gap in measured quantitative nutrient fluxes to the reactive sites in the sediments of rivers. Up to date, this is virtually the only method which can simultaneously capture nutrient and water flux through hyporheic zone within the same device and at the same spatial location. The successful field testing of several devices proved their applicability for quantifying NO_3^- and PO_4^- flux to reactive sites in the hyporheic zone. Hyporheic flux rates of nutrients and denitrification rates measured in an agricultural 3rd order stream were generally in agreement with contemporary alternative measurements and rates reported in literature. Our results clearly highlight the advantages of HPFM compared to commonly used methods, first of all their capability to integrate longer time spans.

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Quantifying nutrient flux to the potentially reactive sites in the hyporheic zone is an essential step to further improve our process based knowledge on hyporheic nutrient cycling. In the future, long-term measurements of nutrient fluxes as obtained from HPFM can feed into and advance the transport part of nutrient cycling models.

We anticipate further improvement and increased use of hyporheic zone passive flux meter approaches in order to advance conceptual models of nutrient cycling in the hyporheic zone. We demonstrated modifications which extended PFM application from groundwater to hyporheic zones. Taking a similar approach, passive flux meters may be adapted for the use in other environments: e. g. lakes, estuaries, etc. While we focused on nutrients, PFMs may also be used for a wide range of other substances like contaminants or trace elements. Their deployment should be considered whenever

- flux instead of concentration is needed
- the focus is on general transport characteristics of a stream rather than short term dynamics,
- the use of sensors is impractical because sensors for the target solute are not available, or the hyporheic environment is not accessible with electronical sensors.

Being labor efficient and attractive with respect to relatively low costs, numerous HPFM can be efficiently used to cover larger areas and assess the degree of local heterogeneity. Further, neither sensitive technology, maintenance, nor power supply are needed which can be extremely advantageous for the use in remote areas or study sites without power infrastructure.

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Figures and tables

Table 1. [illegible]lent Tracers and Partitioning Characteristics

Resident tracers	Aqueous concentration ($g\ L^{-1}$)	
methanol	1.2	4.9
ethanol	1.2	20
Isopropyl alcohol (IPA)	2.3	109
tert-butyl alcohol (TBA)	2.3	309
2,4-dimethyl-3-pentanol (DMP)	1.2	>1000

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Table 2. Selected morphological and hydrological parameters of the testing site. All parameters are averages for the duration of the testing phase from 04.06.2015-11.06.2015

	Surface water	unit	
cross sectional area	A_{SW}	m²	3.41
depth (mean)	h	m	0.565
width (mean)	w	m	6.03
mean velocity	v	m s^{-1}	0.097
discharge	Q_{SW}	m^3 s^{-1}	0.32
NO_3^--N	$C_{NO3\ SW}$	mg m^{-3}	2863
NO_3^--N mass flux	$M_{NO3\ SW}$	mg s^{-1}	896
PO_4^--P	$C_{PO4\ SW}$	mg m^{-3}	165
PO_4^--P mass flux	$M_{PO4\ SW}$	mg s^{-1}	51
	Hyporheic zone upper 50cm		
depth of HZ assessed with HPFM	h_{HZ}	m	0.5
cross sectional area of HZ	A_{HZ}	m²	3.02

Table 3. Summarized parameters of NO_3^- transport and removal through the upper 50 cm of the hyporheic zone at the test site. Values are averages for the testing phase from 04.06.-11.06.2015.

parameter		unit	
water flow through HZ	Q_{HZ}	L s^{-1}	0.0265
% of river water entering HZ	% water HZ	%	0.008
Horizontal Darcy velocity	q_x	cm d^{-1}	76
average NO_3^- concentration in the HZ	$C_{NO3\ HZ}$	mg m^{-3}	1389
% NO_3^- entering the HZ which is denitrified	% denitri in HZ	%	52
potential NO_3^- load entering HZ	$M_{HZ\ theory}$	mg s^{-1}	0.08
NO_3^- load measured in HZ	$M_{HZ\ measured}$	mg s^{-1}	0.037

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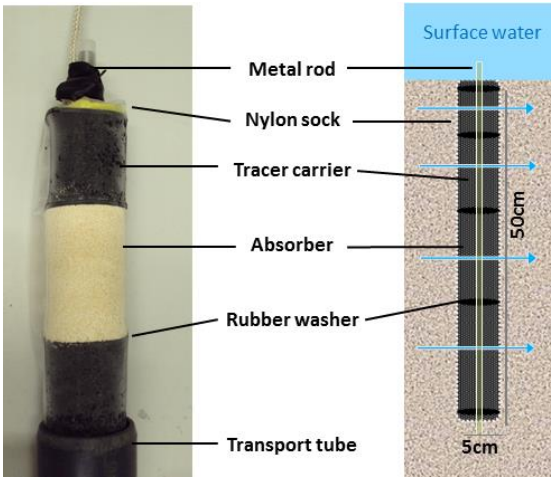

Figure 1. Photograph of an HPFM before deployment (left) and schematic profile of a deployed HPFM (right)

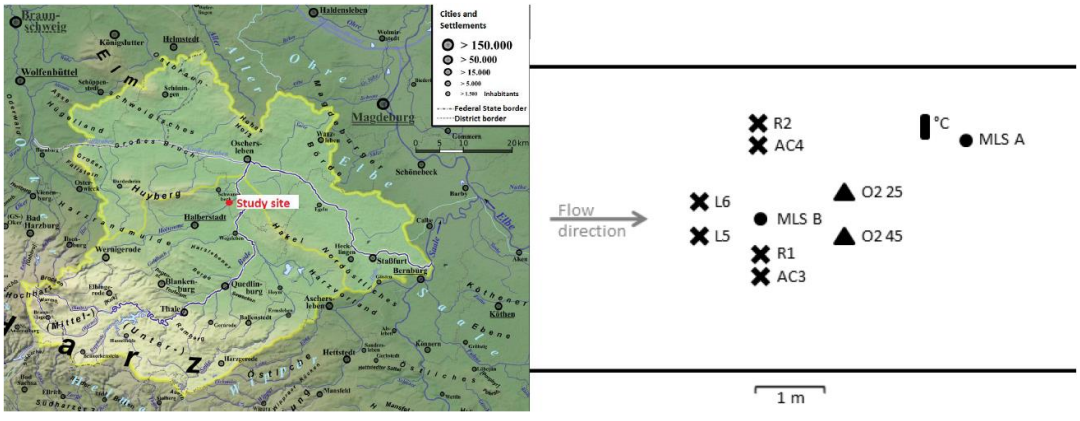

Figure 2. Map of Bode catchment, the study site is marked in red (left) and overview of instrumental setup at the Holtemme for the testing phase in June 2015 (right).

R1, R2 resin only HPFMs; AC3, AC4 activated carbon only HPFMs; L5,L6 alternating layered HPFMs; MLSA, MLSB Multi-level sampler; O2 25, O2 45 subsurface oxygen logger; °C vertical temperature profile

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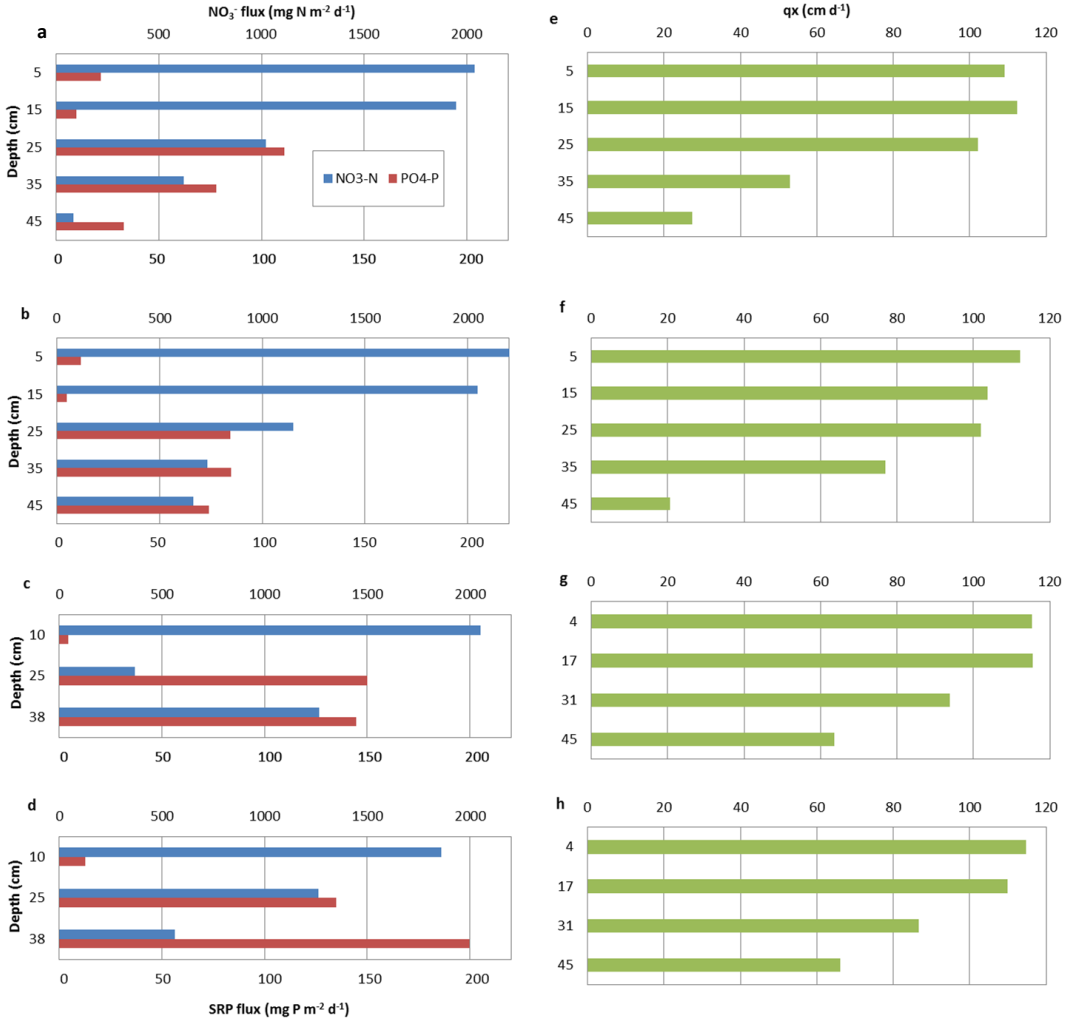

Figure 3. Time integrative measurements for the 04.-11.06.2015. Left side: Horizontal NO_3^--N and SRP-P flux in mg m^{-2} d^{-1} through the resin HPFMs R1 (a), R2 (b) and the layered HPFMs L5 (c) and L6 (d). Right side: corresponding Darcy velocities q_x in cm d^{-1} through the activated carbon HPFMs AC3 (e) and AC4 (f) and the layered HPFMs 5L (g) and 6L (h)

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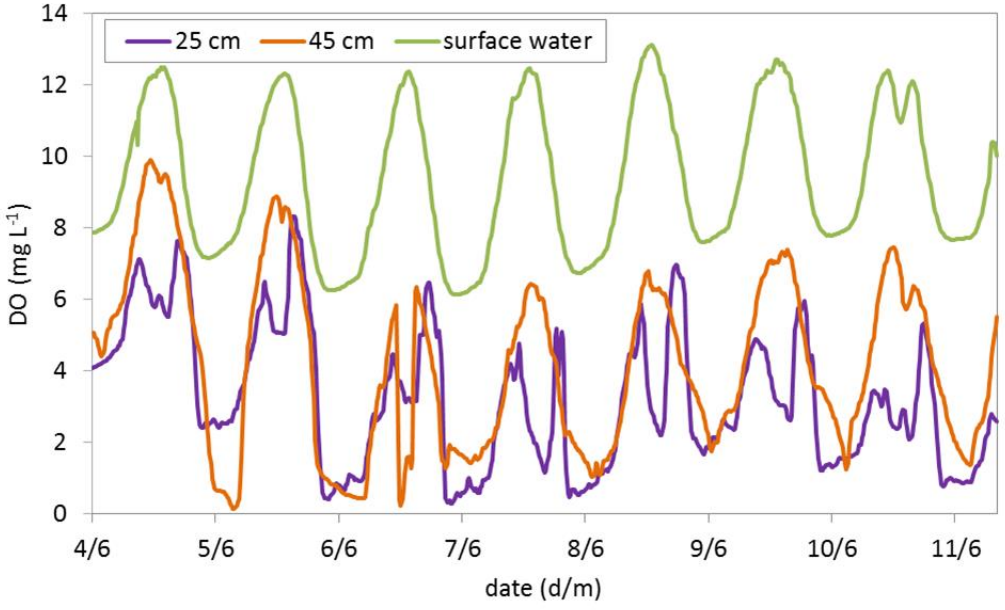

Figure 4. Time series of dissolved oxygen concentrations in the surface water (green) and the subsurface water (depth 25 cm, purple and depth 45 cm orange) at the study site from 04.-11.06.2015

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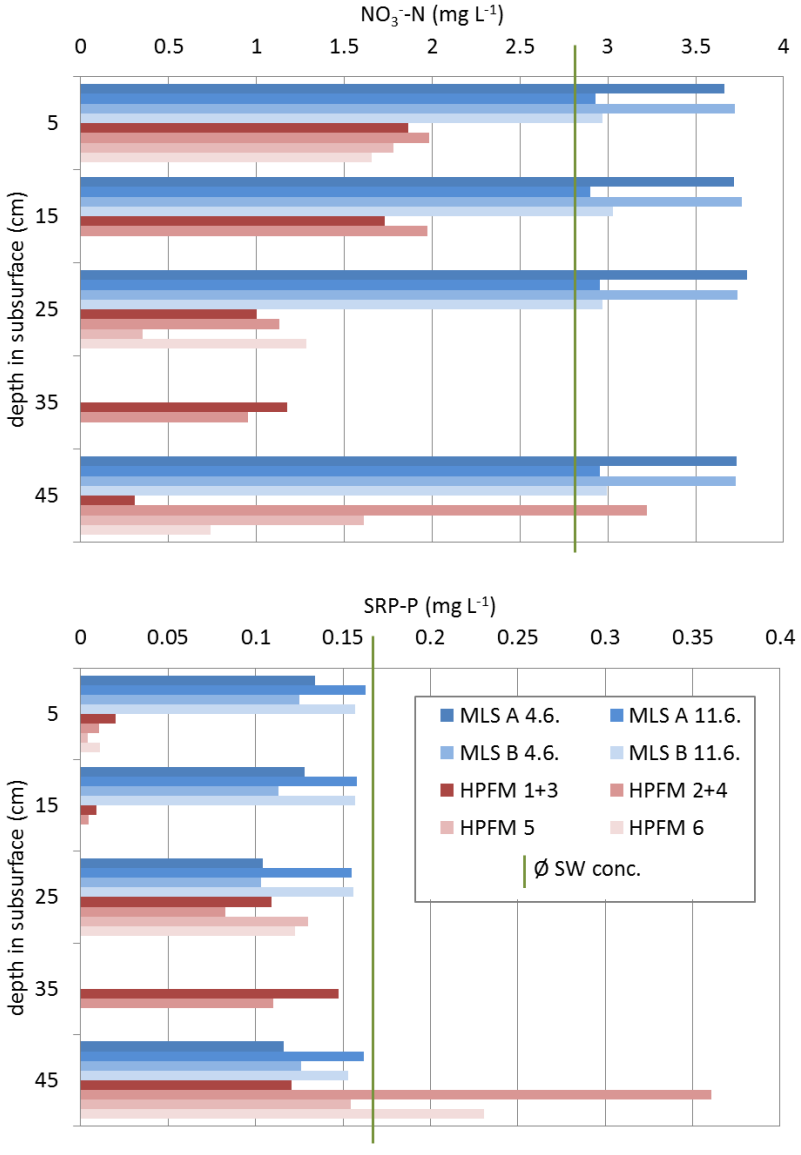

Figure 5. Comparison between manually sampled pore water from MLS (red) and HPFM (blue) for NO_3^--N (top) and SRP-P (bottom). Each MLS was sampled on the 04. and 11.06.2015. Average surface water concentration during the deployment time is marked in green.

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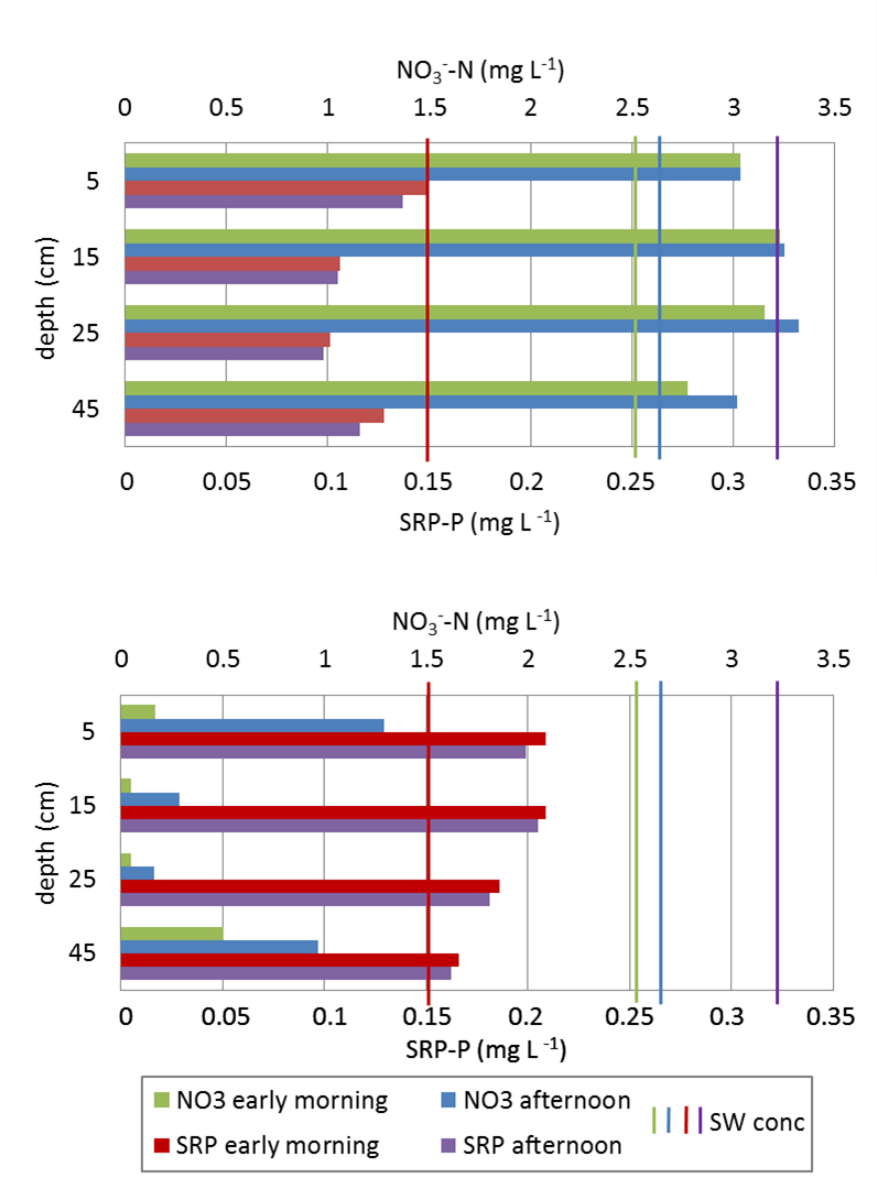

Figure 6. Concentrations of NO_3^--N and SRP in time differentiating manually taken pore-water samples from MLS A (bottom) and MLS B (top) on 8th October 2015. Corresponding surface water concentrations are marked as vertical lines.

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Quantifying nutrient fluxes in Hyporheic Zones with a new Passive Flux Meter (HPFM)

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Abstract. The hyporheic zone is a hotspot of biogeochemical turnover and nutrient removal in running waters. However, ~~due~~nutrient fluxes through the hyporheic zone are highly variable in time and locally heterogeneous. Resulting from the lack of adequate methodologies to ~~methodological constraints~~obtain representative long-term measurements, our quantitative knowledge on ~~nutrient fluxes to those reactive zones~~transport and turnover in this important transition zone is still limited.

In groundwater systems passive flux meters, devices which simultaneously detect horizontal water and ~~nutrient flows~~solute flow through a screen well in the subsurface, ~~proofed to be~~ are valuable tools for ~~load estimates.~~measuring fluxes of target solutes and water through those ecosystems. Their functioning is based on accumulation of target substances on a sorbent and concurrent displacement of a resident tracer which is previously loaded on the sorbent.

Here we ~~present adaptations to~~ evaluate the applicability of this methodology ~~and a smart deployment procedure which allow its use~~ for investigating water and ~~solute~~nutrient fluxes in ~~river sediments. The new~~hyporheic zones. Based on laboratory experiments we developed hyporheic passive flux ~~meter~~meters (HPFM) ~~delivers time integrating values of horizontal hyporheic nutrient fluxes for periods of several days up to weeks. Especially in highly heterogeneous environments like the hyporheic zone, measuring flow and nutrient concentration in a single device is preferable when compared to methods that derive flux estimates from separate measurements of water flows and chemical compounds.~~

~~We constructed HPFMs~~with a length of 50 cm ~~length,~~which were separated in 5-7 segments ~~which allowed~~allowing for vertical resolution of horizontal nutrient and water transport ~~in the range of 10 cm.~~. The results of a seven day ~~long~~ field test, which included simultaneous measurements of oxygen and temperature profiles and manual sampling of pore water, ~~revealed further advantages of the method: While~~ reinforced the need for time integrating measurements of horizontal hyporheic nutrient and water fluxes: Due to the high temporal variability of nutrient fluxes in the subsurface of our study reach, single grab ~~sampling~~samples of pore water could not ~~account~~ be used to characterize overall fluxes. With HPFM cumulative values for the ~~high temporal variability of nitrate fluxes in our~~

~~study reach, HPFMs accumulatively captured reliable values for~~average flux during the complete deployment time~~. Mass balances showed that more than 50 % of the nitrate entering the~~ could be captured, while at the same time reducing the sampling effort. Based on the measurements from this field test we exemplarily show, how HPFM measurements can be used to explore hyporheic ~~zone was removed in the assessed area.~~ denitrification rates and nutrient dynamics. Being low in costs and labor effective, many flux meters can be installed in order to capture larger areas of river beds. ~~The extended application of passive flux meters in hyporheic studies~~This novel technique has therefore the potential to deliver ~~the urgently needed~~ quantitative data which is required to ~~feed into realistic models and lead to a better understanding~~answer unsolved questions about transport and turnover of nutrients in hyporheic zones. A remaining limitation to the method is the potential susceptibility to biofilm growth on the resin, an issue which was not considered in previous passive flux meter applications. Potential techniques to inhibit biofouling are discussed based on the results of ~~nutrient cycling in~~ the ~~hyporheic zone~~presented work.

Keywords: hyporheic exchange, nutrient ~~retention~~fluxes, quantitative methods, running waters, stream metabolism, tracer dilution, ion exchange resin

1 Introduction

~~Northern and central European rivers~~Rivers export high loads of nitrogen from inland catchments to the marine environment. The ecological and economic problems caused by eutrophication of coastal and riverine ecosystems ~~systems~~ have been recognized years ago (Patsch and Radach, 1997; Artioli et al., 2008; Skogen et al., 2014~~;Patsch and Radach, 1997).~~). Decades of nutrient studies have unveiled, that rivers cycle rather than only transport nutrients (Garcia-Ruiz et al., 1998a; Seitzinger et al., 2002; Galloway et al., 2003~~;Garcia-Ruiz et al., 1998a). However, the quantitative dimensions~~). In agriculturally dominated areas, in-stream processes may for example retain up to 38 % of ~~instream dynamics~~nitrate (NO_3^-) and 48% of ~~nitrogen (N) and other nutrients are still not completely understood (Wollheim~~soluble reactive phosphate (SRP) inputs (Mortensen et al~~., 2008;Grant et al., 2014).~~

~~Even though dissimilatory nitrate reduction to ammonium (DNRA) and subsequent anaerobic ammonium oxidation (anammox) might be of importance in some systems (Smith~~, 2016). The hyporheic zone, the subsurface region of streams and rivers that exchanges water, solutes and particles with the surface (Valett et al., 1993) and may mix stream-water during the transport through the sediments with underlying groundwater (Triska et al., 1989; Fleckenstein et al., 2010; Trauth et al., 2014) is one key compartment for instream nutrient cycling (Fischer et al., 2005; Zarnetske et al., 2011b). ~~2015), in most river systems, nitrate (NO_3^-) removal via denitrification~~ For instance, denitrification, the anaerobic reduction of NO_3^- to gaseous N_2 ~~is~~and in most river systems the dominant dissimilatory process which removes N out of the system (Laursen and Seitzinger, 2002; Bernot and Dodds, 2005; Lansdown et al., 2012~~).~~

~~Various studies found that in-stream denitrification~~; Kunz et al., 2016), often exclusively happens at "reactive sites" in the hyporheic zone (Duff and Triska, 1990;~~Rode et al., 2015). The hyporheic zone is defined as the subsurface region of streams and rivers that exchanges water, solutes and particles with the surface (Valett et al., 1993). The occurrence of anaerobic areas, the buffering of~~ Rode et al., 2015). While the importance of the hyporheic zone is

widely acknowledged (Basu et al., 2011; Stewart et al., 2011), unsolved questions remain about the mechanisms and magnitude of hyporheic nutrient transport and turn-over. Up-to now, methodological restrictions impeded quantitative investigations of transport and turnover in this important transition zone (Alexander et al., 2009; Zarnetske et al.,2011b; Grant et al., 2014). Attempts to quantify hyporheic nutrient processing rates have primarily been based on benthic chamber and incubation experiments (Findlay et al., 2011; Kessler et al., 2012). Those laboratory (mesocosm and flume) experiments can estimate the denitrification potential of the substrates, usually via denitrification enzyme assays (DEA). However, the realized denitrification rates are determined simultaneously by environmental and hydrological conditions rather than by substrate type or denitrification potential alone (Findlay et al., 2011). Small scale fluctuations in hyporheic flow and metabolic activity can additionally influence the redox conditions and thereby the binding and mobilization of highly sorptive nutrients such as phosphorous. Due to those natural variations ~~in flow, temperature or water chemistry, a continuous supply with nitrate and carbon provide a benign habitat for denitrifying microbes (Garcia-Ruiz et al., 1998b;Opdyke~~and the complexity of environmental conditions, hyporheic transport of nutrients cannot satisfactorily be mimicked in artificial set-ups (Cook et al., 2006;~~Alexander et al., 2009;Zarnetske et al., 2011a). As a result of much higher residence times hyporheic transient storage was recognized to have a stronger influence on overall removal of NO_3^- and other nutrients like phosphate (P) when compared to surface water storage zones (Basu et al., 2011;Stewart et al., 2011). However, even in nitrogen saturated systems like agriculturally impacted groundwater and streams, denitrification can~~ Grant et al., 2014). Finally, hydrological processing and physical storage of nutrients can be ~~limited by NO_3^- availability, because consumption in the hyporheic zone is faster than resupply of solutes (Fischer et al.,~~ more important than biological uptake capacity (Runkel, 2007; Brookshire et al., 2009;~~Böhlke~~ Covino et al., ~~2009;O'Connor and Hondzo, 2008;Harvey et al., 2013).~~ 2010): In addition, to remove nutrient loadings at larger time scales (e. g. seasonal or annual), intermediate storage disperses the propagation of pollutant spikes which could be harmful for receiving water bodies (Findlay et al., 2011). ~~In stagnant waters, such as lakes, the transport of dissolved nutrients to the sediments is dominantly controlled by diffusion. Therefore, surface water concentrations~~For those reasons, it is of interest to quantify the amount of nutrients ~~are a good predictor for uptake processes and potential limitations (Dillon and Rigler, 1974;Jones and Bachmann, 1976). In rivers, hydrological processing and physical storage of nutrients were found to be as important or of even higher importance than biological uptake capacity (Covino et al., 2010;Runkel, 2007;Brookshire et al., 2009), because the transport of solutes~~actually reaching the reactive sites in the subsurface collateral to ~~reactive sites is determined by advection rather than diffusion (Grant et al., 2014;Wörman et al., 2002). As a result, it is not possible to interpret hyporheic processing rates from surface water observations, if subsurface fluxes and transport velocities are unknown. Nutrient flux (i.e. the product of nutrient concentration and specific discharge) is conclusively a much better metric for hyporheic turnover rates than concentration alone.~~the processes they undergo there (Seitzinger et al., 2006; Zarnetske et al., 2012).

Several numerical ~~or~~and empirical models demonstrated the complexity of surface – subsurface exchange of water and solutes. Exchange rates could be attributed to surface flow, water level, sediment properties and various other hydrological, biological, chemical and physical factors (~~Trauth et al., 2015;Boano et al., 2014;~~Böhlke et al., 2009~~).~~

While NO_3^- has been the main focus of hyporheic nutrient studies, in-stream P cycling has recently received increasing interest (; Boano et al., 2014;Mulholland Trauth et al., 2009). Even though2015).

In addition to this multitude of influencing factors, the earliest studiestemporal variability and local heterogeneity of hyporheic nutrient dynamics focused on P (Mulholland and Webster, 2010;Hall et al., 2009), only very few studies have attempted to directly assess P transport in the hyporheic zone (Boano et al., processes often cause high uncertainties in2014). Based on the fact that the mobility, transformation and retention of phosphate (PO_4^-) are mainly dependent on redox conditions which are directly coupled with NO_3^- concentrations (Smith et al., 2011;McDaniel et al., 2009;Gabriel et al., 2006) hyporheic transport studies should address NO_3^- and phosphate fluxes simultaneously.

Small changes in stream state or water chemistry variables were found to significantly alter hyporheic zone nutrient processing. Hence quantitative models are fraught with high uncertainties while. However, due to the lack of adequate techniques, experimental investigations of nitratenutrient turnover rates in the hyporheic zone are rare and often exclusively of qualitative nature (Grant et al., 2014;Mulholland et al., 1997; Grant et al., 2014).). As a result, for both, N and P, there is urgent need for quantitative measurements of nutrient flux through the hyporheic zone: On one hand, to support the modelled results (Alexander et al., 2009;Boyer et al., 2006;Wagenschein and Rode, 2008), on the other hand, to provide a solid basis for the discussion on the importance of hyporheic processes in whole stream NO_3^- uptake (Fischer et al., 2009). While the importance of subsurface pathways for N cycling is widely acknowledged (Seitzinger et al., 2006;Zarnetske et al., 2012), there is still disagreement on the amounts of nutrient loadings actually reaching the reactive sites in the subsurface (Fischer et al., 2005;

Our Zarnetske et al., 2011b).

Whilst understanding of surface water NO_3^- cycling in streams has remarkably improved in the recent years, benefiting from newly emerging sensors whichthat deliver high resolution time series of nutrient concentrations in the surface water (Pellerin et al., 2009; Hensley et al., 2014; Rode et al., 2016a; Rode et al., 2016), equivalent technics are not available for subsurface studies. Here, tracer injections and /or manual sampling are still the only approach for observing the fate of NO_3^- and other nutrients (Fischer et al., 2009;Ingendahl et al., 2009;USEP, 2013). Nutrient 2016b). Similarly, nutrient uptake measurements based on whole stream tracer injections and mass balances (Böhlke et al., 2009;McKnight et al., 2004; Böhlke et al., 2009) have been used for determining general uptake dynamics on the reach scale, but did not identify the reaction sitessites (hyporheic versus in channel or algal canopies) or specific local uptake processes (Ensign and Doyle, 2006; Ruehl et al., 2007). More important, in-stream measurements do exclusively account for water which is re-infiltrating into the main stem after passage through the hyporheic zone. Under loosing conditions, where most of the surface water nutrient-influx is flowing towards the groundwater, processing rates in the hyporheic zone cannot be observed in the surface water. Likewise, if groundwater is contributing significantly to surface water chemistry, surface water mass balances do not characterize nutrient cycling in the hyporheic zone realistically (Trauth et al., 2014).(Trauth et al., 2014). However, for the long-term assessment of hyporheic processes and their contribution to the overall cycling observed in surface water monitoring, adequate techniques are not available. In the subsurface, separate assessment of water flow

velocities and subsequent grab sampling are the only approaches for quantifying the fate of nutrients (Fischer et al., 2009; Ingendahl et al., 2009; USEP, 2013). Exchange rates are traditionally assessed via hydraulic head differences or tracer injections (Fleckenstein et al., 2010; USEP, 2013). High resolution vertical temperature profiles have efficiently been used to derive vertical Darcy velocity (q_v) (m d^{-1}) in the streambed. This method is based on time series measurements of temperature in the stream and in the sediments at several depths. Based on a numerical model, vertical flow velocities can then be calculated from the measured attenuation and phase shift of the diurnal temperature signal which, at depth, varies with the vertical hyporheic flux (Keery et al., 2007; Schmidt et al., 2014). While measurements of vertical Darcy velocities are a valuable asset and have been used as supplement in this study, horizontal fluxes are also needed in order to assess hyporheic transport and residence time (Binley et al., 2013; Munz et al., 2016). Active heat-pulse tracing enables highly resolved in situ measurements of direction and velocity of hyporheic flow (Lewandowski et al., 2011; Angermann et al., 2012). These methods are valuable in shallow sediments (max.15-20 cm) and rivers with fine sediments, but may not be implementable in streams with coarser sediments.

~~Other attempts are based on benthic chamber and incubation experiments (Kessler et al., 2012;Findlay et al., 2011). Those laboratory or mesocosm and flume experiments deliver rates~~Independ of ~~denitrification potential of the substrates, usually assessed via denitrification enzyme assays (DEA). Nevertheless, it was found that the realized denitrification rate is determined by environmental and hydrological conditions rather than by substrate type or denitrification potential (Findlay et al., 2011). Likewise would small scale fluctuations in hyporheic~~ how water flow ~~and metabolic activity influence the redox conditions and thereby the binding and mobilization of phosphorous. Due to those natural variations and the complexity of environmental conditions, hyporheic transport of nutrients cannot satisfactorily be mimicked in artificial set ups (Cook et al., 2006). Hence, those attempts neglect many important hydrological, biophysical and chemical processes that influence the nutrient fate and transport (Grant et al., 2014). Separately measuring exchange rates via hydraulic head differences or tracer injections and~~is measured, pore water nutrient concentrations have ~~often been the methods of choice~~ to be assessed in addition in order to determine hyporheic nutrient fluxes (Saenger and Zanke, 2009; Alexander et al., 2009). ~~These methods~~ Manual pore water grab samples, usually extracted with drive points, provide valuable insights into the time specific conditions at the target site. However, hyporheic zone processes are highly variable in time and space (Cooke and White, 1987), ~~which can lead to high uncertainties if separated measurements are used to characterize a single parameter (e. g. nutrient flux). Additionally, attempting to characterize larger areas with these methods or account for short term variability is laborious and costly. However, as long as~~so that if grab sampling is not repeated at high frequencies it ~~can~~is exclusively ~~be interpreted as~~ a snap shot which does not allow a characterization of the system. Only repeated sampling at high frequencies and over longer timespans as conducted for example by Duff et al. (1998) may account for the short term variability. Attempting to characterize larger areas with these methods is laborious and costly. Conclusively, ~~long~~ new, affordable and efficient methods for the long-term ~~measurements~~ measurement of integrative nutrient fluxes through the hyporheic zone are required to ~~obtain an integrative mass flux signal.~~improve model development (Boyer et al., 2006; Wagenschein and Rode, 2008; Alexander et al., 2009) and determine the site specific extent of nutrient processing in the hyporheic zone (Fischer et al., 2009).

Measuring solute fluxes through porous media is also ~~aspired~~of interest in groundwater studies. There, passive flux meters (PFM) have successfully been used to quantify fluxes of dissolved nutrients (Cho et al., 2007) and contaminants (Hatfield et al., 2004; Annable et al., 2005; Verreydt et al., 2013~~;Hatfield et al., 2004~~) through screened groundwater monitoring wells. ~~PFMs~~PFM allow ~~determination of the~~determining horizontal water flux through the screened media from the ~~dilution~~displacement of ~~a~~ resident ~~tracer and to simultaneously capture the amount of~~tracers which are previously loaded on a sorbent. Simultaneously transported target ~~solute~~solutes (nutrient or contaminant) are captured using a permeable sorbent. Observation time can range from days to weeks~~, so that the time averaged solute flux during that defined period can be monitored. A~~. Also, a method for quantifying vertical mass flux through sediments (SBPFM) has recently been developed and field testing has been initiated (Layton, 2015~~)~~).

~~For~~In this study we evaluate the ~~application~~applicability of ~~PFMs~~PFM for the measurement of horizontal nutrient fluxes in hyporheic zones. We hypothesized that, while the principal concept of PFM can be maintained, several adaptations ~~are~~will still be necessary~~.~~: Most importantly, the flow velocities and the masses of transported solutes are expected to be ~~several~~ orders of magnitude higher in hyporheic zones than in ~~the~~ groundwater. Thus, a suitable sorbent for the target nutrients with ~~appropriately~~ high loading capacity ~~is~~was required. The market of anion absorbing resins, originally manufactured for water purification purposes, is ~~huge~~large and offers a wide range of products with varying characteristics (Annable et al., 2005; Clark et al., 2005). Various criteria, like possible interference of resin compounds with the resident tracer analysis or the hydraulic conductivity of the resin have to be considered depending on the study site and research ~~question~~questions.

Additionally, a new deployment and retrieval procedure ~~has~~had to be developed, because contamination with surface water has to be impeded. Corrections for convergence and divergence of flowlines into or around the flux meter have been established in earlier studies (Klammler et al., 2004). However, accounting for an impermeable outer casing of a flux meter is much more complicated and requires additional factors which have to be determined experimentally for each specific application (Hatfield et al., 2004; Klammler et al., 2004; Annable et al., 2005). ~~avoided. In~~For hyporheic studies we therefore intended to deploy the passive flux meter ~~should be~~ in a way that allows direct contact with the surrounding sediments ~~with a~~and minimal manipulation of the natural flow pattern. Furthermore, ~~PFMs~~PFM have so far been used ~~in waterbodies which were not subjected to light or high temperatures and~~ for contaminants other than nutrients (Annable et al., 2005; Verreydt et al., 2013; Layton, 2015) or in groundwater where nutrient concentrations were low (Cho et al. 2007)~~.~~ Hence, biofouling on the meters was not regarded in previous studies~~.~~, but was considered as a potential challenge in our application.

~~In this study~~Here we present ~~the~~a modification of the passive flux meter for applications in the hyporheic zone (Hyporheic Passive Flux Meter, HPFM) ~~with the example~~and results of a first field test for hyporheic N and ~~in~~P fluxes in a nutrient rich 3rd order stream (Holtemme, Germany) with a strong anthropogenic impact gradient (Kamjunke et al., 2013~~)~~).

2 Methods

2.1. Construction and materials

The Hyporheic Passive Flux Meters (HPFM) consisted of a nylon ~~sock~~mesh which was filled with a mixture of a macroporous anion exchange resin as a nutrient absorber and ~~a~~alcohol tracer loaded ~~carrier.~~activated carbon (AC) for the water flow quantification. In the present study ~~we~~HPFM were constructed ~~them in a~~ 50 cm long~~.~~ and 5 cm ~~Ø cylindrical form.~~in diameter. A stainless steel rod in the middle assured the stability of the device (**Figure 1**).

To ~~detect~~measure vertical ~~gradients~~profiles of horizontal fluxes of both nutrient and water ~~fluxes~~ in the hyporheic zone, the HPFM was divided into several segments ~~by~~using rubber washers. Steel tube clamps were used to attach the nylon ~~sock~~mesh to the steel rod placed in the center of the HPFM. The nylon mesh ~~for the socks~~ was purchased from Hydro-Bios (Hydro-Bios Apparatebau GmbH, Kiel-Holtenau, Germany) and is available in a wide range of mesh size and thicknesses. We used a mesh size of 0.3 mm. ~~A~~In general, meshes should be as wide as possible because very fine mesh may act as a barrier to water flow limiting infiltration of water and solutes into the HPFM (Ward et al., 2011). However, the mesh should be smaller than the finest sediments, AC or resin granules. As final step, a rope was connected to the tube clamp on the upper end of the HPFM in order to facilitate retrieval.

2.~~1.1. Preparation of activated carbon~~

~~**Similar to the groundwater PFM, silver impregnated activated carbon (AC) was used as sorbent for the resident tracers. The AC used for the HPFM in this study was provided by the University of Florida, Gainesville**~~2. Selection and ~~**was prepared as reported (Annable et al. 2005). By choosing the same manufacture as used in the above mentioned studies, we could rely on physical and chemical**~~ characterization ~~**and calculated retardation factors for alcohol tracer partitioning behavior which have been established by Hatfield et al. (2004) and Annable et al. (2005).**~~of resin

~~The magnitude of water flow through the flux meter is unknown in the field applications, therefore multiple resident tracers with a wide range of tracer elution rates were used (Hatfield et al., 2004;Cho et al., 2007). An alcohol tracer mixture for approximately 10 HPFM was prepared by combining 100 mL of methanol, 100 mL of ethanol, 200 mL of isopropanol (IPA), 200 mL of tert-butanol (TBA) and 66 mL of 2, 4-dimethyl-3-pentanol (2,4 DMP) (Cho et al., 2007).~~

~~For an aqueous solution of resident alcohol tracers, a standard ratio of 13 mL tracer mixture was transferred to 1 L water in a Teflon sealed container and was then shaken by an automated shaker over a period of several hours. Subsequently, 1.5 L of dry activated carbon was added to the aqueous tracer solution and rotated for 12 hours to homogenize the AC tracer mixture. Following mixing, the AC tracer mixture was stored in a sealed container and refrigerated.~~

2.1.2. Deployment and retrieval procedure

HPFMs were built, stored and transported in 70 cm long standard polyethylene (PET) tubes (58 x 5.3 SDR 11) purchased from a local hardware store (Handelshof Bitterfeld GmbH, Bitterfeld, Germany). To avoid resident alcohol tracer loss, the transport tubes with the HPFMs were sealed with rubber caps and cooled during storage and transport.

On site, prior to installing, the HPFMs were transferred to a stainless steel tube (5.3 cm inner diameter) with a loose steel drive point tip on the lower end. The steel casing and HPFM were driven into the river bed using a 2 kg hammer until the upper end of the HPFM was at the same level as the surface-subsurface interface. The metal casing was retrieved while the HPFM was held in place using a steel rod.

After a specific period of exposure, the HPFM was retrieved by holding the transport tube in place and quickly drawing the HPFM into the tube using the rope fixed to the upper end of the HPFM. The required length of the transport tube, steel drive casing and retrieval rope was determined by the depth of the water level in the stream. After retrieval, the HPFMs were transported to the laboratory, where they were removed from the transport tube for sampling. Each segment was cut open and the sorbent mixture was recovered, homogenized and a subsample transferred to 40 mL glass vials.

2.2. Analysis and data treatment

2.2.1. Water flux

The AC samples were shipped to the University of Florida for analysis. In the laboratory, the tracer mass in standard AC samples and the tracer mass remaining in the final AC samples were extracted by iso-butyl alcohol (IBA). About 10 g of AC samples were collected into pre-weighed 40 mL vials containing 20 mL IBA. Vials were rotated on a Glas-Col Rotator, set at 20 % rotation speed, for 24 h. Then, subsamples were collected in 2 mL GC vials for alcohol tracer analysis. The samples were analyzed by a GC-FID (Perkin Elmer Autosystem) (Cho et al. (2007).

The relationship between time average specific discharge q through the device and tracer elution is given by the equation (1) (Hatfield et al., 2004)

$$q = \frac{1.67\, r\theta\, (1-M_R)\, R_d}{t} \quad (1)$$

where r (m) is the radius of the HPFM, θ is the water content in the HPFM ($m^3\ m^{-3}$), M_R is the relative mass of tracer remaining in the HPFM sorbent, t is the sampling duration and R_d is the retardation factor of the resident tracer on the sorbent.

The retardation factor R_d is a measure for the rate of elution of a particular alcohol from the AC. R_d for the specific set of tracers and AC used in this study had previously been determined by the relationship between tracer mass loss and the cumulative water flow by Hatfield et al. (2004) and Annable et al. (2005) (**table 1**).

~~2.2.2. Nutrient flux~~

~~All values~~Values for NO_3^- and ~~PO_4^-~~SRP in this article ~~are noted as~~refer to NO_3^--N or ~~PO_4^-~~SRP -P respectively~~ if not indicated otherwise.~~.

~~NO_3^- and PO_4^- were extracted and analyzed in the laboratory at UFZ in Magdeburg, Germany.~~

~~For extraction, 30 mL of 2M KCl was added to 5 g of resin and rotated for 24hours. The solution was then analyzed on a Segmented Flow Analyser Photometer (DR 5000, Hach Lange): NO_3^--N at 540 nm (precision of 0.042 mg L^{-1}), SRP at 880nm (precision 0.003 mg L^{-1}).~~

~~The time-averaged advective horizontal nutrient flux can be calculated by the following relationship (Hatfield et al., 2004):~~

~~$J_N = \frac{qM_N}{2\alpha\pi Lt}$ (2)~~

~~Where M_N (kg) is the mass of nutrient adsorbed, L (m) is the length of the vertical thickness of the segment, α ( ) is a factor that characterizes the convergence or divergence of flow around the HPFM.~~

~~2.3. Laboratory experiments~~

~~All~~ The experiments described in this ~~paragraph~~chapter were accomplished on triplicate samples~~, if not indicated otherwise~~. Reported values are averages of these triplicates and standard deviations (std) between those three values.

Instrumental precisions refer to the limits of detection (LOD) as stated by the manufacturers.

The nutrient sorbent had to meet the following criteria:

~~a)~~ Have a high loading capacity for NO_3^-, PO_4^- and competing anions

~~b) Be~~(1), be free of compounds which could interfere with the alcohol tracer measurements (e.g. organic substances) (2) and have a low background of NO_3^- and PO_4^- (3).

~~c) Have a low background of NO_3^- and PO_4^-~~

A pre-selection for anion-absorbing resins which were free of organic compounds was made based on information provided by the manufacturers (Purolite®, Lewatit®, Dowex®).

2.2.1. Nutrient background

Nutrient background on the resins was ~~then~~ determined by extracting and analyzing NO_3^- and PO_4^- from each resin. Therefor 30 mL of 2M KCl was added to 5 g of each pure resin ~~as described above. Extractable~~and rotated for 24 hours. The solution was then analyzed on a Segmented Flow Analyser Photometer (DR 5000, Hach Lange) for NO_3^- at 540 nm (precision 0.042 mg L^{-1}) and for SRP at 880 nm (precision 0.003 mg L^{-1}). In order to estimate the effect of background concentrations on final results in the actual field application of HPFM, the extractable background concentrations were then converted to nutrient fluxes using a Darcy flux of ~~45 mm h~~q_v = 4 m d^{-1}, an estimate ~~of~~based on hyporheic flow ~~velocity based on prior~~velocities which were measured previously with salt tracer tests at

the study ~~side~~site. Likewise, the expected hyporheic nutrient flux was computed from previously examined concentrations in pore water samples and ~~above-mentioned hyporheic flow.~~ the Darcy flux. The only resin with nutrient background below 5 % of expected concentrations was Purolite® A500 MB Plus (Purolite GmbH, Ratingen, Germany), which had ~~–~~extractable background NO_3^- of 8 µg NO_3^-~~-N~~ g^{-1} wetted resin (std = 1.6 µg g^{-1}) and 0.08 µg PO_4^{3-}~~-P~~ g^{-1} resin~~.~~ (std = 1.7 × 10^{-3} µg g^{-1}). Purolite® A500 MB Plus was then considered for ~~further~~ testing the loading capacity. The limit of quantification *LQ* for the nutrient extraction resulting from this background was calculated according to the EPA Norm 1020B (Greenberg et al., 1992) as the sum of background concentration and 10 times the standard deviation and amounted to 24 µg NO_3^- g^{-1} resin and 0.097 µg PO_4^{3-} g^{-1} resin.

2.2.2. Loading capacity

Purolite® A500 MB Plus is a macroporous polyvinylbenzyl-trimethylammonium exchanger in the chloride form with a typical granular size of 0.88 mm diameter, an average density of 685 g L^{-1} and an effective porosity of 63 %. The theoretical absorbing capacity is indicated in the product sheet as 1.15 eq L^{-1} (molar weight equivalences per liter of resin), corresponding to 71.3 g NO_3^- L^{-1}. Assuming hyporheic flow velocities of q_x = 4 m d^{-1} and a concentration of 10 mg NO_3^- L^{-1} the volume of one HPFM could adsorb NO_3^- for 89 days. However, if multiple anions are present, real loading capacities for NO_3^- are expectedly lower.

For the determination of ~~the~~a realistic loading capacity, three 5 cm diameter columns were filled to a height of 5 cm with wetted Purolite® A500 MB Plus resin, placed in a vertical position and infiltrated with water collected from the study reach. The columns were covered with tin foil to keep ~~out light~~them dark and ensure stable temperature. A constant supernatant of 1 cm was kept on all three columns~~.~~ in order to ensure uniform infiltration at the surface of the column. Water was continuously pumped (peristaltic pump, ISMATEC® BVP Standard, ISM444) through the columns from top to bottom for 22 days at a speed of 20 mL h^{-1}, which also equals the expected Darcy velocity of ~~45 mm h~~q_x = 4 m d^{-1}. River water was supplied from a 22 L HDPE canister (Rotilabo® EPK0.1). SRP and NO_3^- concentrations in this reservoir were revised daily. The draining water at the bottom outlet of the columns was sampled twice a day and analyzed for SRP and NO_3^-~~.~~.

Biofilm growth on the resin was assessed by repeating the same experiment in smaller columns and extending it for several days after break-through occurred. That way, nutrient consumption by biofilm after the exhaustion of the loading capacity could be monitored. ~~Additionally,~~ After the experiment we colored samples of resin granules ~~were colored~~ from the columns with SybrGreen ($C_{32}H_{37}N_4S^+$) on nucleic acid and examined them under a confocal laser scanning microscope~~,~~ in order to depict the degree of bacterial fouling on the granular surface.

~~Concurrent to~~

2.3. Preparation of activated carbon with alcohol tracers

As designed for the ~~resin,~~groundwater PFMs, silver impregnated activated carbon (AC) was used as sorbent for the resident alcohol tracers. The same AC as in previous PFM applications (Annable et al., 2005) was used for the HPFM in this study and was provided by the University of Florida, Gainesville. The AC had a bulk density of 550 g L^{-1}, a grain size ranging from 0.42 to 1.68 mm and a hydraulic conductivity k = 300 m day^{-1}.

Since the magnitude of water flow through the flux meter is unknown a priori, multiple resident tracers with a wide range of tracer elution rates were needed. The retardation factor of a substance R_d is a measure for the rate of elution of the substance from a particular carrier. Alcohols offer a wide range of retardation factors and can easily be mixed and sorbed to the AC (Hatfield et al., 2004; Cho et al., 2007). By choosing the same manufacturer for the AC and the same alcohol mixture as used in the above mentioned studies, we could rely on physical and chemical characterizations and calculated R_d for alcohol partitioning behavior which have been established by Hatfield et al. (2004), Annable et al. (2005) and Cho et al. (2007) (**table 1**).

An alcohol tracer mixture for approximately 10 HPFM was prepared by combining 100 mL of methanol, 100 mL of ethanol, 200 mL of isopropanol (IPA), 200 mL of tert-butanol (TBA) and 66 mL of 2, 4-dimethyl-3-pentanol (2,4 DMP).

In order to prepare the resident alcohol tracers on the AC, the AC was soaked in an aqueous solution containing the resident alcohol tracers. A standard ratio of 13 mL tracer mixture was added to 1 L of water in a Teflon sealed container and was then shaken by an automated shaker over a period of several hours. Subsequently, 1.5 L of dry activated carbon was added to the aqueous tracer solution and rotated for 12 h to homogenize the AC tracer mixture. After mixing, the supernatant water was discarded and the AC tracer mixture was stored in a sealed container and refrigerated, preventing the evaporation of the alcohol tracers

Similarly to the resins, the AC was tested for background nutrients by extraction with 30 ml ~~KCL~~KCl per 5 g AC. The activated carbon contained 0.01 mg PO_4^{-} ~~-P~~ g^{-1}AC (std = 7.5×10^{-4} mg g^{-1}) and 0.08 mg NO_3^{-} ~~-N~~ g^{-1} AC, (std = 5×10^{-3} mg g^{-1}), which amounts ~~up~~ to 75 % of the expected concentration for nitrate and 320 % for SRP. To investigate whether the AC could be cleaned by washing, we repeatedly treated AC samples with distillated water or KCl as depicted in the extraction description above. Nutrients did not leach ~~of~~off under water treatment and neither did KCl treatment satisfactorily reduce extractable background concentration on the AC. After the third washing of AC with KCl, ~~still~~ 0.02 mg PO_4^{-} ~~-P~~ (std = 3.3 ×10^{-4} mg g^{-1}) and 0.04 mg NO_3^{-} ~~-N~~ (std = 2.3×10^{-3} mg g^{-1}) could still be extracted per g AC. Further, it ~~is~~was unclear to which degree replacing absorbed nutrients by KCl would alter the alcohol tracer retardation and extraction on the AC. For those reasons ~~it was~~, we decided to keep the nutrient absorbing resin separated from the AC. As AC did not release background nutrients under water treatment, water flowing first through AC and afterwards resin layers was not considered problematic.

2.5. Analysis and data treatment

After field installation, an exposure period and retrieval, the HPFMs were transported to the laboratory, where they were they were sampled for analysis. One segment after the other was cut open and the sorbent was segment-wise recovered, homogenized and a subsample transferred to 40 mL glass vials. The subsamples from resin segments

were then analyzed for nutrient content, the subsamples from AC segments were analyzed for the remaining alcohol tracers as described in the following paragraphs.

2.5.1. Water flux

The AC samples were shipped to the University of Florida for analysis. In the laboratory, the mass of the previously applied mixture of alcohol tracers in standard AC samples and the tracer mass remaining in the final AC samples were extracted with iso-butyl alcohol (IBA). About 10 g of AC samples were transferred into pre-weighed 40 mL vials containing 20 mL IBA. Vials were rotated on a Glas-Col Rotator, set at 20 % rotation speed, for 24 h. Then, subsamples were collected in 2 mL GC vials for alcohol tracer analysis. 4The samples were analyzed with a GC-FID (Perkin Elmer Autosystem) (Cho et al.,2007).

The relationship between time averaged specific horizontal discharge q_x (m s^{-1}) through the device and tracer elution is given by equation (1) (Hatfield et al., 2004)

$$q_x = \frac{1.67\, r\theta\, (1-M_R)\, R_d}{t} \quad (1)$$

where r (m) is the radius of the HPFM, θ is the volumetric water content in the HPFM (m^3 m^{-3}), M_R (-) is the relative mass of tracer remaining in the HPFM sorbent, t (s) is the sampling duration and R_d (-) is the retardation factor of the resident tracer on the sorbent.

2.5.2. Nutrient flux J_N

NO_3^- and PO_4^- were extracted and analyzed in the laboratory at UFZ in Magdeburg, Germany, similarly to the analysis of background concentrations on the resin: subsamples of 5g resin were treated with 30 mL of 2 M KCl each and rotated for 24h for extraction. The solution was then analyzed as described above.

The time-averaged advective horizontal nutrient flux J_N (mg m² d^{-1}) can be calculated using the following relationship (Hatfield et al., 2004):

$$J_N = \frac{q_x M_N}{2\alpha r L t} \quad (2)$$

where M_N (kg) is the mass of nutrient adsorbed, L (m) is the length of the vertical thickness of the segment and α (-) is a factor ranging from 0 to 2 that characterizes the convergence ($\alpha > 1$) or divergence ($\alpha < 1$) of flow around the HPFM. If, like in the case presented here, the hydraulic conductivity of the HPFM sorbent (resin or AC) is much higher than of the surrounding and the HPFM is in direct contact with the sediments (i.e. in absence of an impermeable outer casing or well wall), α can be estimated after Strack and Haitjema (1981)

$$\alpha = \left(\frac{2}{1+\frac{1}{K_D}}\right) \quad (3)$$

where $K_D = k_D\, k_0^{-1}$ is the dimensionless ratio of the uniform hydraulic conductivity of the HPFM sorptive matrix k_D (L T^{-1}) to the uniform local hydraulic conductivity of the surrounding sediment k_0 (L T^{-1}). For more details on the correction factor α and applications where a solid casing is required or the permeability of the surrounding sediments is higher than of the device see Klammler et al. (2004) and Hatfield et al. (2004)

2.6. Field testing of hyporheic passive flux meters (HPFMs)

~~2.4~~6.1. Study site

A 30 m long stretch of the Holtemme River, a 3rd order stream in the Bode catchment, TERENO Harz/Central German Lowland Observatory, served as study site (51°56'30.1"N, 11°09'31.8"E~~) (figure 3~~). The testing reach is located in the lowest part of the river, where the water chemistry is highly impacted by urban effluent and agriculture (Kamjunke et al., 2013). Long stretches have been subjected to changes in the natural river morphology by canalization (~~Sachsen-Anhalt~~ Landesbetrieb für Hochwasserschutz und Wasserwirtschaft Sachsen-Anhalt, 2009). The ~~sediment~~sediments at the selected site ~~is mainly~~are sandy with gravel and ~~stones mixing in.~~small cobbles. Sieving of sediment samples delivered the effective grain size d_{10}= 0.8 mm and a coefficient of uniformity C_u = 3.13. The effective porosity n_{ef} is 13 %. After Fetter (2001) the intrinsic permeability can be estimated to K_i = 96 m² and the hydraulic conductivity to k = 81 m day^{-1} Clay lenses are present in the deeper sediments below 35 cm. Mean discharge in the stream is 1.35 m³ s^{-1} with highest peaks around 5-6 m³ s^{-1}. Discharge is continuously recorded by the local authorities at the gauge Mahndorf, 15 km upstream of the testing site. In the course of the year, NO_3^- ~~N~~ concentrations in the lower Holtemme vary between 2 and 8 mg NO_3^- ~~N~~ L^{-1}(~~LHW~~Hochwasservorhersagezentrale, 2015/2016).

~~2.4.2. HPFM testing~~

The equipment was installed for a period of 7 days from 4th to 11th June 2015 as illustrated in **figure 2**.

2.6.2. Deployment and retrieval procedure

HPFM were built, stored dry and transported in 70 cm long standard polyethylene (PET) tubes (58 x 5.3 SDR 11) purchased from a local hardware store (Handelshof Bitterfeld GmbH, Bitterfeld, Germany). To avoid resident alcohol tracer loss, the transport tubes with the HPFMs were sealed with rubber caps and cooled during storage and transport. On site, prior to installation, the HPFMs were transferred to a stainless steel tube, 5.3 cm inner diameter with a loose steel drive point tip on the lower end. The diameter of the steel tube for installation tightly fitted with the rubber washers at the top and bottom end of the HPFM, so that vertical water flow through tube and HPFM during installation was inhibited. The steel casing and HPFM were driven into the river bed using a 2 kg hammer until the upper end of the HPFM was at the same level as the surface-subsurface interface. The metal casing was retrieved while the HPFM was held in place using a steel rod.

After 7 days of exposure, the HPFMs were retrieved by holding the transport tube in place and quickly drawing the HPFM into the tube using the rope fixed to the upper end of the HPFM. The required length of the transport tube, steel drive casing and retrieval rope was determined by the depth of the water level in the stream.

After retrieval, the HPFMs were transported to the laboratory, where they were removed from the transport tube and sampled as reported above.

2.6.3. HPFM testing

Based on the laboratory results for the nutrient backgrounds, and the consequent necessity to keep resin and AC separated two approaches for constructing and deploying ~~HPFMs~~HPFM were ~~field~~ tested in the field.

A) Resin only and AC only HPFMs

4 HPFMs were constructed of which 2 contained only resin (R1 and R2) and the other two contained only AC (AC3 and AC4). The HPFMs were then installed in pairs: AC only and resin only next to each other with a separation distance of 30 cm. Those 4 HPFMs were sectioned in 5 horizontal flow segments, each with a vertical length of 10 cm.

For the calculation of the nutrient flux through each segment of R1 and R2, we used the corresponding water flux through the respective segment of AC3 and AC4.

B) Alternating segments of AC and resin HPFMs

HPFMs L5 and L6 consisted of 7 segments starting and ending with an AC segment and ~~interjacent~~adjacent segments altering between resin and AC (also see **figure 1**). Each segment had a length of 7 cm.

For the calculation of the nutrient flux through the resin segments we used the interpolated water flow measured in the two adjacent AC segments.

~~A control HPFM equal to the HPFMs with alternating segments~~One additional HPFM with alternating layers was used as a control HPFM, in order to assess potential tracer loss or nutrient contamination during storage, transport and deployment/retrieval. This control was stored and transported together with the other HPFMs. After deploying the control HPFM, it was immediately retrieved, transported back to the laboratory and stored until it was sampled and analyzed along with the other HPFMs. The results from the control HPFM also include uncertainties arising from sample storage, analytical processing and the background concentration of nutrients on the resin. Measurements of the other HPFMs were corrected by subtracting the transport, storage and deployment related tracer loss and nutrient accumulation detected in the control.

2.6.4.~~3.~~ Additional measurements

Vertical Darcy velocity (q_v)

The vertical vector of hyporheic Darcy velocities q_v were measured supplementary to the horizontal fluxes assessed with the HPFM in order to estimate the general direction of flow (upwards or downwards) and to calculate the angle of hyporheic flow.

The vertical Darcy velocity (q_v) (m d^{-1}) in the streambed was calculated using temperature profiles measured between January 2015 and October 2015. According to Schmidt et al. (2014~~))~~, vertical flow velocities can be computed from the temporal shift of the daily temperature signal in the subsurface water relative to the surface water. A multi-level temperature sensor (Umwelt- und Ingenieurtechnik GmbH, Dresden, Germany) was installed at

the test site in January 2015. Temperature was recorded at the surface-subsurface interface and at depths of 0.10, 0.125, 0.15, 0.2, 0.3 and 0.5 m in the sediment at a 10 min interval (accuracy of 0.07 °C over a range from 5 to 45 °C~~, and a resolution of 0.04 °C)~~ and a resolution of 0.04 °C). A numerical solution of the heat flow equation was then used in conjunction with Dynamic Harmonic Regression signal processing techniques for the analysis of these temperature time series. The coded model was provided by Schmidt et al. (2014).

Oxygen profiles

~~Two~~We monitored the subsurface oxygen concentration as a primary indication on the redox status of the hyporheic zone in order to evaluate the potential for NO_3^- reduction and PO_4^- mobilization. Therefor two oxygen loggers (miniDO$_2$T, Precision measurement engineering Inc.) incorporated into steel tubes acuminated at the lower end were installed in the river bed ~~at~~. The tubes had filter-screens at the measuring depths of 25 and 45 cm below surface-subsurface boundary. Installation was carried out 4 weeks prior to the experiments, allowing enough time for re-equilibration of the surrounding media. The measurement time step was 5 min.

Multi-level samplers (MLS)

Pore water nutrient concentrations were measured to substantiate the HPFM results. Multi-level samplers as described in detail by ~~(~~Saenger and Zanke (2009~~)))~~ are devices for the manual extraction of hyporheic pore water from several distinct depths. The two samplers A and ~~C~~B used in these experiments were manufactured by the institutional workshop of the UFZ. Like the oxygen loggers both MLS were installed 4 weeks prior to the experiment. They consisted of an outer stainless steel tube with a length of 50 cm and a diameter of 5 cm. Ceramic filters were inserted in this outer steel mantle marking the extraction depths at 5, 15, 25 and 45 cm. The inner sides of the filters were attached to steel pipes that ran to the top of the sampler so that Teflon tubes could be attached. A protective hood was threaded on the upper end of the sampler to preclude particles and sediment entrance. ~~Pore~~ Per sampler and depths 10 mL of pore water was manually extracted by connecting ~~syringes~~a syringe to the open end of the Teflon ~~tubes~~tube and slowly sucking up water at a rate of 2 mL min^{-1}. The 4 extraction depths were sampled successively, always starting with the shallowest depths and continuing with ascendant depths. Manual pore water samples were taken on the 4th and 11th of June 2015, both times between 1 pm and 4 pm local time.

~~A sample volume of about 10 mL was~~ The samples were filtered in the field through a 0.45 µm membrane filter and placed in boro-silica glass vials for transport to the laboratory. Analysis for NO_3^-~~,~~, SRP, sulphate (SO_4^{2-}) and ~~Boron~~boron (B) were conducted in the central analytical ~~department~~laboratory of the UFZ~~.~~, Magdeburg, Germany. Analytical procedure for NO_3^- and SRP was done according to the description above.

SO_4^{2-} and B were used as natural tracers for groundwater and surface water respectively. SO_4^{2-} was analyzed on an ion chromatograph (ICS 3000, ThermoFisher, former DIONEX), B was analyzed on an inductively coupled plasma mass spectrometer (ICP-MS 7500c, Agilent~~)~~). As NO_3^- and SRP concentrations in the pore water samples taken on June 4th and 11th 2015 were unexpected and inconsistent with results from the HPFMs, the sampling was repeated on the 8th of October. The aim of this repeated sampling was to investigate whether diurnal variations in subsurface NO_3^- and SRP concentrations could explain the discrepancies between MLS and HPFM results. In October, both MLS were sampled twice, the first time in the early morning before sunrise and again in the early afternoon (around

2 pm). Those samples were analyzed for NO_3^-, SRP and SO_4^{2-}. Due to technical issues, boron could not be measured in October.

~~Manual pore water samples were taken twice during the installation period of the HPFM: on the 4th and 11th of June 2015, both times between 1 pm and 4 pm local time.~~

~~Due to conflicting findings in the pore water samples taken on June 4th and 11th 2015, the sampling was repeated on the 8th of October. In October, each device was sampled twice, the first time in the early morning before sun rise and again in the early afternoon (around 2 pm).~~

~~-~~Surface water chemistry ~~was~~

Surface water concentrations of SRP and NO_3^- were monitored ~~with two sets of sensors: upstream and downstream of the reach. For this~~in order to compare surface and subsurface water chemistry. Therefor we installed an automated UV absorption ~~sensors~~sensor for NO_3^- (ProPS WW, TriOS) ~~on~~at the beginning of the testing reach ~~and 1.5 km downstream~~ for the duration of the experiments. The pathway-length of the optical sensor was 10 mm, measuring at wavelengths 190-360 nm with a precision of 0.~~03mg~~03 mg NO_3^- ~~-~~ -N L^{-1} and an accuracy of ± 2 %. The measurement time step was set to 15 min. SRP, SO_4^{2-} and B concentrations in the surface water were assessed with grab samples taken simultaneously to the MLS measurements.

~~Both~~The UV ~~sensors were~~sensor was supplemented with a multi-parameter probe YSI 6600 V2/4 (YSI Environmental, Yellow Springs, Ohio) recording the following parameters: pH (precision 0.01 units, accuracy ± 0.2 units), specific conductivity (precision 0.~~001mS~~001 mS cm^{-1}, accuracy ± 0.5 %), dissolved oxygen (precision 0.01 mg L^{-1}, accuracy ± 1%), temperature (precision 0.01 °C, accuracy ±0.15 °C~~,~~) and turbidity (precision 0.1 NTU, accuracy ± 2 ~~%) and chlorophyll a (precision 0.1 µg L^{-1}, linearity: R^2>0.9999 relative to dilution of Rhodamin WT solution of 0 to 400 µg L^{-1}~~). ~~%~~).

~~2.4.4. Nitrate transport and denitrification~~

~~Flux and denitrification~~

2.6.5. Exemplary estimation of nitrate turnover

Estimates for hyporheic removal activity R_N for the specific conditions at the study site during the HPFM testing phase were calculated using the morphological and hydrological parameters summarized in **table 2.**

The ~~proportion~~absolute amount of water ~~infiltrating~~passing the screened area of the hyporheic zone ~~was then calculated as the ratio $\frac{Q_{HZ}}{Q_{SW}}$. Where~~ Q_{HZ} ($m^3\ s^{-1}$) is the product of the average horizontal vector of the Darcy velocity q_x ($m\ s^{-1}$) measured in the HPFM and the cross sectional area of the upper 50 cm of the hyporheic zone A_{HZ} (m^2).

The proportion of water infiltrating the hyporheic zone $\%Q_{HZ}$ (%) was then calculated from the ratio $\frac{Q_{HZ}}{Q_{SW}}$, where Q_{SW} ($m^3\ s^{-1}$) is the average discharge at the study site during the days of measurements, derived from continuous records at the gauche Mahndorf, which were provided by the local authority Landesbetrieb für Hochwasserschutz und Wasserwirtschaft Sachsen-Anhalt.

The NO_3^- removal activity of the hyporheic zone R_N (%) was calculated from the difference in average surface water concentration $C_{NO3\text{-}SW}$ (mg NO_3^- L^{-1}) and the average concentration observed in the HPFM ~~($C_{NO3\text{-}HZ}$).~~ (mg NO_3^- L^{-1}), were $C_{NO3\text{-}HZ}$ is the quotient $\frac{J_N}{q_x}$.

3. Results

3.1. Laboratory experiments

3.1.1. Loading capacity and biofouling

Break-through in the sorbent column experiments occurred after 300 pore volumes (PVs) or 21 days at selected drainage for both NO_3^- and SRP. ~~The minimal absorbing capacity as calculated from parameters indicated in the product sheets of Purolite® A500 MB Plus was 265 PVs, equaling 19 days in the described set up.~~

In the biofouling experiment, the NO_3^- concentration in the draining water gradually decreased again after ~~beak~~break-through. SRP in the draining water was completely depleted 6 h after the break-through. The calculated amount of retained nutrient in comparison to manufacturer value loading capacities of Purolite® A 500MB Plus indicate that the absorbing capacity of the resin in this small column experiment was exhausted after 25.5 hours (APPENDIX A). We attributed the decrease of nutrients in the draining solution after breakthrough to biotic consumption of SRP (limiting nutrient) and NO_3^-. Under the laser scanning microscope growth of biofilm could be observed on obviously brown stained Purolite® beads of the columns from the biofouling experiment and to a very low degree on beads from the same column which appeared still clean (APPENDIX A). Browning of Purolite® beads was not observed on Purolite® beads from the loading experiment (bigger columns, experiment not extended after break through) but on the top 2 cm of the HPFM R2 after exposure at the study site.

~~Under the laser scanning microscope growth of biofilm could be observed on all of the examined Purolite® beads.~~

3.2. Field testing

3.2.1. HPFMs and additional measurements

HPFMs

Deployment required approximately 15 min per HPFM and could be conducted by two persons. The water depth during the installation was 40 to 100 cm, depending on the specific location in the stream. ~~The results from the control HPFM proved that tracer loss or nutrient accumulation during transport, deployment and retrieval was negligible.~~

The average horizontal water flow q_x and nutrient flux J_N measured in the HPFM during the 7 day field testing are illustrated in **figure 3**. All flux meter except 5L showed declining ~~concentrations~~J_N and q_x with depth. Average horizontal q_x was 76 cm d^{-1}, ranging from 115 cm d^{-1} in the shallowest layer of 5L to 20 cm d^{-1} in the deepest layer of AC4~~)~~. Nutrient fluxes of 4.2 mg NO_3^- m^2 d^{-1} (std = 0.1 mg m^2 d^{-1}) and 5.2 mg SRP m^2 d^{-1} (std = 0.9 mg m^2 d^{-1}) were detected in the control HPFM. Comparing these fluxes to the J_N values measured with the other HPFM, an

average 0.3 % of the uncorrected NO_3^- flux and 5 % of the uncorrected SRP flux were attributed to tracer loss or nutrient accumulation resulting from transport, deployment, retrieval, analytical processing of samples and the background concentrations on the resin.

~~With an average water flux of Q_{HZ} = 2.65 e^{-5} m^3 s^{-1} through the assessed upper 50 cm of the hyporheic zone and across the 6 m width of the stream, 0.008 % of water transported in the river entered the hyporheic zone **(table 3)**. While the average surface water concentration was 2.86 mg NO_3^--N L^{-1}, the average concentration in the subsurface measured with the~~ Vertical Darcy velocity (q_y)

~~**HPFMs** was only 1.39 mg NO_3^--N L^{-1}. Accordingly, 52 % of the infiltrating NO_3^- was removed in the hyporheic zone. For SRP the average surface water concentration from 4th to 11th June 2015 was 0.165 mg PO_4^-P L^{-1}, the average concentration in the hyporheic zone was 0.11 mg PO_4^-P L^{-1}.~~

~~Temperature profile~~

Vertical water flow q_y in the stream bed was predominantly downward from January to October 2015. It was ~~continuously~~exclusively downward during the HPFM testing phase, ranging from 40 to 55 cm d^{-1}. ~~The relation~~With this, vertical flow q_y was slightly lower than average horizontal flow q_x. Resulting from the relationship between q_y and q_x ~~($\tan\alpha = \frac{q_y}{q_x}$) results in an approximate~~the angle of hyporheic flow ~~of~~($\tan\alpha = \frac{q_y}{q_x}$) was 32° downwards~~, assuming that q_x is directed downstream~~.

Oxygen profiles

We observed strong diel variations in oxygen concentration in the hyporheic zone. During several nights oxygen was nearly depleted (**figure 4**).The minima and maxima oxygen concentration in the subsurface occurred contemporarily with the respective extremes in the surface water. Interestingly the amplitude in DO oscillation was higher at 45 cm depths than at 25 cm depths.

Multi-level samplers

~~The results from the manual pore-water sampling conducted in June 2015 are illustrated in **figure 5.**~~ In order to facilitate direct comparison, nutrient fluxes as measured in the HPFM were converted to flux ~~average~~averaged concentrations ~~using~~which are the ~~measured~~quotient of J_N and the respective q_x.

~~In general~~ (**figure 5**). Overall, nutrient concentrations in the manually sampled pore~~-~~ water taken in June 2015 were higher than the average concentration derived from the HPFM. ~~The~~While the expected increase of SRP and decrease of NO_3^- and water flow with depths was observed in the HPFM, ~~whereas~~ pore water extracted with the MLS showed no change over depth ~~for~~ neither ~~of~~for NO3$^-$ nor SRP. In the ~~two substances~~repeated manual pore water samples taken in October (**figure 6**) NO_3^- concentrations were uniformly lower in the early morning than in the afternoon, whereas SRP behaved the other way round. This trend was consistent in both samplers even though the average concentration and distribution over depths differed between the samplers A and B.

~~Observations during installation and retrieval of the HPFM suggest that HPFM L6 and R4 hit a clay lens in the lowest segments (deeper that 35 cm in the subsurface).~~

On both sampling dates in June (04.06. and 11.06.2015) neither SO_4^{2-} nor ~~B~~boron showed a vertical gradient in concentrations in the pore water samples. SO_4^{2-} concentrations of 170 mg L^{-1} on the 4th June and 190 mg L^{-1} on the 11th June were in the same range ~~than~~as surface water concentrations. Likewise were ~~B~~boron concentrations with 50

to 60µg L^{-1} ~~in~~ consistence with the concentrations in the surface water. ~~Conclusively, manually sampled hyporheic zone~~In October, SO_4^{2-} concentrations in the pore water ~~was originating exclusively from the~~samples were in the range of surface water concentrations, slightly declining with depth.

~~The repeated manual pore~~ We conclude from these findings that manually sampled hyporheic zone water ~~sampling in October (**figure 6**) showed clear differences in SRP and NO_3^- concentration between early morning and afternoon. NO_3^-~~ was not influenced by groundwater, as the concentrations ~~in the subsurface were in general higher in the early morning hours than in the afternoon. SRP shows the opposite trend: higher~~ of SO_4^{2-} and boron would then differ significantly from surface water concentrations ~~in the early morning~~.

Surface water ~~NO_3^- concentrations on~~chemistry

Temperature, O_2 and pH showed the expected diurnal amplitudes whereas specific conductivity and NO_3^- did not display a distinct diurnal pattern (**table 4**).

3.2.2. Estimates of turnover rates

With an average water flow of Q_{HZ} = 2.65 ×10^{-5} m^3 s^{-1} through the assessed upper 50 cm of the hyporheic zone and across the 6 m width of the ~~sampling day were 2.5 mg NO_3^- N L^{-1}~~stream, 0.008 % of water transported in the ~~morning and 2.7~~river entered the hyporheic zone (**table 3**).

While the average surface water concentration was 2.86 mg NO_3^- L^{-1}, the average concentration in the subsurface measured with the HPFM was only 1.39 mg NO_3^- ~~N~~ L^{-1} ~~in the afternoon. SRP concentrations were consistently 0.15~~. Assuming that the difference between surface and subsurface concentration arose from hyporheic consumption of infiltrating NO_3^-, the average removal rate R_N was 52 %. For SRP the average surface water concentration from 4th to 11th June 2015 was 0.165 mg PO_4^- L^{-1}, the average concentration in the hyporheic zone was 0.11 mg PO_4^- L^{-1}.

4. Discussion

The application of the HPFM ~~proved as an innovative tool~~ for ~~the~~ quantitative in situ measurement of horizontal NO_3^- and SRP fluxes through the hyporheic zone~~. Earlier applications of~~ is novel. An earlier study on passive flux meter (SBPFM) in river ~~bed studies~~beds (Layton, 2015) ~~exclusively~~only assessed vertical flow~~, so that this is the first study which used HPFM for the quantification of horizontal nutrient transport in the hyporheic zone. (Layton, 2015)~~ of contaminants and is therefore not comparable to the application presented here. In the current work, adaptations were developed, tested and improved. Those include the choice of an appropriate resin, assessment of biofilm growth on the instruments and ~~a practice~~an approach that avoids challenges with contamination of the ~~absorber with~~ sorbent ~~inherited~~with nutrients. ~~While both~~The results from the control HPFM showed that the uncertainty in measurement related to handling of the HPFM and processing of ~~the latter-mentioned practices examined~~samples as conducted in this study ~~delivered reliable results,~~is acceptable. Finally, the minimum and maximum deployment time will depend on the Darcy velocity and nutrient concentrations at a study site. Since the values derived from the control incorporate all the processing steps of HPFM and samples, they can be regarded as

the method detection limit *MDL* (Greenberg et al., 1992). The *MDL* defines the lower limit for the use of HPFM in cases where nutrient fluxes are very low and deployment time cannot be extended. We recommend that a control HPFM is incorporated in each field application of HPFM in order to determine the specific *MDL*. The upper limit is given by the loading capacity of the resin or complete displacement of all resident alcohol tracers.

The high nutrient background on the AC required the separation of resin and AC in the HPFMs. We tested two different HPFM designs in this study, of which each inherits designated characteristics being more or less beneficial for different specifications~~.~~.

~~1) Deploying two HPFMs of which~~: The first approach, pairs of two HPFM where one is used to assess the water flux and the second to capture nutrients~~. This approach~~ is preferable if a ~~high resolution~~ highly resolved depth profile is needed (a heterogeneous horizontal flux ~~distribution~~ in the vertical direction). Since this approach assumes that local horizontal heterogeneity is negligible in the range of 20-30 cm, we recommend this type only for the use in uniform systems such as channelized river reaches.

~~2)~~ ~~Alternating nutrient absorbing~~ Even in those systems however, small scale variability in stream bed and sediment characteristics can cause spatially heterogeneous flow distributions (Lewandowski et al., 2011; Mendoza-Lera and Mutz, 2013). The second approach with alternating nutrient sorbents and water flux measuring segments is ~~a good choice if local lateral flux heterogeneity is expected to be high and/or if~~therefore preferable in most other cases as long as a high resolution over the vertical profile is ~~moderately heterogeneous~~not required. In general, several HPFM should be grouped together in order to obtain representative results.

Further improvements of the HPFM for nutrient studies in the subsurface of rivers could be achieved by identifying a nutrient free carrier for the tracers. First, because this would allow measuring nutrient and water flux at the same location within the device and thereby increase spatial resolution. Second, because in a mixed texture of nutrient absorber and tracer carrier the antibacterial nature of the activated carbon would suppress biofouling on the absorbent. ~~Here we showed that~~We observed substantial biofilm growth ~~occurred~~ on the resin in the laboratory ~~as well as under~~and on the top 2 cm of the field ~~conditions. Even though the observations on~~ deployed HPFM R2. The results of the column experiments suggest that biofilm growth on the resin porous media did not affect its loading capacity~~, it is unclear, to what extent the biofilm bound nutrients can be captured by the implemented extraction procedure. As a result, it is not possible to completely exclude that biofouling might lead to underestimation of actual nutrient flux through the HPFMs.~~ and that biofilm growth only started after the loading capacity of the tracer was exhausted. R2 detected higher NO_3^- fluxes in the top layer than the other HPFM. This could be due to contamination of the top layer of this HPFM with surface water (if the HPFM was not introduced sufficiently deep into the sediments). The further implication would be, that this layer was exposed to much higher water and nutrient infiltration, so that the loading capacity was exhausted before the end of the experiment allowing biofilm accumulation. At the current state it is unclear, to what extent the biofilm bound nutrients can be extracted by the procedure used here. Further experiments would also be needed to clarify under which conditions biofilm growth can occur and if bacterial uptake, transformation and release of nutrients influence the concentrations of nutrients inside the HPFM. HPFM segments on which biofilm is visible should be interpreted with caution. Finally,

identifying a procedure or materials which completely inhibit biofouling will be an important step in the further development of HPFM.

In addition to instrumental adaptations we presented an installation ~~practice~~procedure, which allows for smooth deployment with minimal disturbance of the system. Unlike typical well screen deployments where ~~PFMs (~~PFM (Annable et al., 2005; Verreydt et al., 2013~~; Annable et al., 2005~~) or SBPFM (Layton, 2015) have been inserted into a screened plastic or steel casing, our technique enabled the direct contact of the ~~HPFMs~~HPFM with the surrounding river sediments. ~~Compared~~Thereby, the integration of the HPFM in the natural system is improved and the generation of artificial flow paths along the wall of the device is avoided. As a result, the disturbance created by the HPFM is low compared to other intrusive measurements of hyporheic flow~~, the disturbance created by a HPFM is low, because the measuring~~ like piezometer or salt tracer injection. Additionally, the HPFM include a measurement time that is long relative to the duration of the installation. ~~By removing the solid casing, we further improved the integration of the instrument in the natural system and avoid the generation of artificial flow paths along the walls of the device. For~~While the installation of mini-drive points or heat pulse sensors in sediments coarser than sand may be difficult or even impossible and also proved unfeasible at our field site, installation of the HPFM with the presented technique was successful. The correction for convergence of flowlines into the device or divergence around it is relatively simple and already incorporated in the equation for the flux calculation. We believe that it is applicable for a wide range of field conditions. However, for very coarse sediments, a protection of the HPFM with a ~~screened plastic or steel casing~~solid screen might still be ~~preferential.~~ preferred. If fine particles are observed to bypass the mesh and enter the HPFM, a finer mesh should be chosen. We did not observe clogging of the mesh or intrusion of particles at our study, though in highly permeable systems with fine particle transport this might have to be considered.

A mayor ~~gain~~advantage of the HPFM method is highlighted by the findings of the 7 day long field testing: ~~Concurrent~~In June, we found discrepancies between the average concentrations measured in the HPFM and the concentration found using the MLS. From our measurements it is not possible to prove that the HPFM results are correct and the MLS results biased. Nevertheless, the HPFM showed the expected decline in J_N with depths, whereas the MLS pore water concentrations were similar at all depths. This can be related to two reasons: First, we might have sampled surface water which bypassed along the wall of the MLS. The question would then be why that happened in June but not in October. Second, we might have sampled the MLS at a time point when the hyporheic zone was inactive in respect to nutrient processing. Considering the high diurnal amplitudes in hyporheic oxygen concentration, we assumed that the discrepancy between HPFM and MLS arose from oscillations in hyporheic nutrient concentrations similar to the oxygen pattern. Microbial consumption of O_2 in the sediments is commonly found in nutrient rich streams (Harrison et al., 2005; Nimick et al., 2011) and may be the triggering factor for night time denitrification in the hyporheic zone (Christensen et al., 1990; Laursen and Seitzinger, 2004; O'Connor and Hondzo, 2008). The redox conditions in the subsurface may also regulate the mobilization/demobilization of phosphate (Smith et al., 2011). The repeated manual sampling of pore- water from ~~MLSs~~MLS in October showed diurnal variations of SRP and NO_3^- in the subsurface of the testing reach~~. Whereas, as in the first MLS assessment in June 2015 only a single time specific snap shot sampling was conducted, the results may not realistically represent~~

~~the overall conditions at the target site. Diurnal~~, supporting the hypothesis that diurnal cycles in benthic metabolism ~~cause~~caused temporal variations in ~~various water quality parameters, including many nutrients~~hyporheic SRP and NO_3^- concentrations at our study site. As the majority of sampling is commonly conducted during daylight hours, night time conditions are underrepresented in studies relying on single manual sampling events. ~~That flux~~ Flux average concentrations can ~~derivate~~deviate by more than 50 % from estimates based on single event sampling. as was illustrated by comparison between our manual samples and the average pore- water concentrations calculated from the HPFM data.

~~We consider that a combination of~~ Repeated pore water ~~samples for~~sampling at high frequencies can be used to determine diurnal dynamics ~~and~~. However, continuing this over a longer time span is laborious, whereas if only few single time specific snap shot samplings are conducted, the results may not realistically represent the overall conditions at the target site. Our comparison between MLS and HPFM reinforce the need for long term recording of nutrient transport through the hyporheic zone ~~via HPFM is~~. In general, most of our knowledge on hyporheic nutrient dynamics is based on measured surface water dynamics and models which project these dynamics on hyporheic processing. Theoretically, we could measure nutrient fluxes in the hyporheic zone and estimate whole stream uptake rates from these measurements. However, the substantially higher effort to obtain subsurface data is not justified in most cases. As long as the overall in-stream retention is the focus, surface water monitoring will remain the method of choice. Innovative tracer experiments may even allow quantifying hyporheic exchange in streams. Haggerty et al. (2009) proposed a "smart" tracer approach, where the injected substance resazurin converts irreversibly to resofurin under metabolic activity. While a promising tool for detecting metabolic activity at the sediment-water interface in streams, first, uncertainties about sorption and transformation characteristics of these tracers remain (Lemke et al., 2013) and second, those methods give no evidence about nutrient transport to those reactive sites.

Thus, whenever the nutrient processing function of the hyporheic zone and its quantitative contribution to stream nutrient retention is of interest, for example in the evaluation of restauration measures including a rehabilitation of the river bed, direct measurements of hyporheic fluxes are indispensable. The HPFMs are a valuable approach that can be efficiently used to characterize and quantify nutrient dynamics in a sediment system. ~~Presumably, for our field test, the lower NO_3^- concentrations in the subsurface in the early morning hours compared to afternoon samples detected in the MLS samples in October can be attributed to a dominance of night time denitrification. DO exhibited strong diurnal cycles with anoxic periods occurring in the subsurface during night times periods. This temporal pattern, owing to microbial consumption of O_2 in the sediment, is commonly found in nutrient rich streams (Nimick et al., 2011;Harrison et al., 2005) and identified as triggering factor for night time denitrification in the hyporheic zone (O'Connor and Hondzo, 2008;Laursen and Seitzinger, 2004;Christensen et al., 1990). Presumably, the redox conditions in the subsurface also regulated the mobilization/demobilization of phosphate (Smith et al., 2011). Reducing conditions during night periods enhanced the mobilization of PO_4^-. During day elevated O_2 and NO_3^- concentrations suppressed the reduction of Fe^{3+} (Miao et al., 2006), PO_4^- was therefore demobilized and SRP was decreasing (Gabriel et al., 2006). Accordingly, SRP concentration in hyporheic pore water samples was higher in the early morning than in the afternoon. Concurrent~~We consider that a combination of HPFM, MLS and concurrent measurements of pore water oxygen concentrations, as presented in this study ~~are therefore essential~~, provide a

practical set-up to interpret ~~nutrient dynamics. To our knowledge there is a lack of studies which examine the diurnal pattern of nutrients in the hyporheic zone and no studies which actually measured them.~~hyporheic nutrient dynamics.

Like solute concentrations and water flow patterns, the vertical extension of the hyporheic zone varies in time and space and between different rivers and reaches. Our set~~-~~-up assessed exclusively the upper ~~50cm~~50 cm of the hyporheic zone. We found continuously degreasing NO_3^- concentrations with depths, suggesting that this entire area (and potentially deeper) of the subsurface contained active sites for denitrification. While ~~some studies have found~~it was stated that denitrification is limited to the upper few cm of the hyporheic zone close to the sediment-water interface (Hill et al., 1998; Harvey et al., 2013), our results are in accordance to findings by Zarnetske et al. (2011b) and Kessler et al. (2012) who also report extended active hyporheic zones. ~~As~~Conducting collateral tracer tests, as suggested for example by Abbott et al. (2016), could deliver further evidence and characterize distinct flow paths. Nevertheless, since vertical water movement was ~~constantly~~overall downward and the lowest concentrations of NO_3^- were observed in the deepest segments of the ~~HPFMs,~~HPFM, it is very likely that the hyporheic zone at ~~this~~our study site ~~likely~~ extends deeper than the 50 cm evaluated. The length of an HPFM can easily be increased, depending on the individual site conditions.

Considering the high spatial heterogeneity of the hyporheic zone, a larger number of HPFM would be needed to derive reliable and statistically supportable rates of hyporheic nutrient dynamics. The following example aims to display further possibilities of interpreting HPFM measurements. At our study site, the hyporheic removal potential R_N of more than 50 % of infiltrating NO_3^- and 30 % of SRP ~~is clearly an indication of~~ suggests an active hyporheus. Evaluation of the effect of hyporheic denitrification activity on overall ~~nitrate~~NO_3^- removal in the stream or the normalization of hyporheic uptake to a benthic area requires the length of the hyporheic flow path, which can be derived from the residence time of water and solutes in the hyporheic zone τ_{HZ} and the horizontal Darcy velocity q_x. Assuming a downward flow direction, τ_{HZ} could be inferred from the vertical Darcy velocity q_y as assessed from the temperature profiling and the hyporheic zone depths of 50 cm. Thereafter, τ_{HZ} conceptually corresponds to the time the water travels through the hyporheic zone before exiting to groundwater and s_{HZ} to the horizontal vector of the flow paths. The denitrification rate $U_{NO3\text{-}HZ}$ (mg NO_3^--N m^{-2} d^{-1}) is then the difference between the theoretically transported NO_3^- mass $M_{NO3\text{-}HZ\ theor}$, which is the product of Q_{HZ} and $C_{NO3\text{-}SW}$ and the measured mass flux $M_{NO3\text{-}HZ\ real}$. During the testing phase $U_{NO3\text{-}HZ}$ was calculated as 693 mg NO_3^- ~~N m^{-2} d^{-1}. The same procedure yields a removal rate for SRP of $U_{PO4\text{-}HZ}$ = 24 mg PO_4^- P m^{-2} d^{-1}~~ m^{-2} d^{-1}. The same procedure yields a removal (uptake or adsorption) rate for SRP of $U_{PO4\text{-}HZ}$ = 24 mg PO_4^- m^{-2} d^{-1}. Calculating $U_{NO3\text{-}HZ}$ in the same way for each single depth assessed with the HPFM can deliver additional information about vertical gradients on nutrient processing rates and help to identify the most active depth in hyporheic zone. $U_{NO3\text{-}HZi}$ of a particular layer in the hyporheic zone can be derived by the differences in uptake rate between the regarded layer and the overlying layer. For instance the removal rates attributed to the different layers of HPFM L6 would be $U_{NO3\text{-}HZ15}$ = 567 mg NO_3^- m^{-2} d^{-1} in the shallow layer (0 to 15 cm depths), $U_{NO3\text{-}HZ30}$ = 174 mg NO_3^- m^{-2} d^{-1} in the layer from 15 to 30 cm depths and $U_{NO3\text{-}HZ45}$ = 256 mg NO_3^- m^{-2} d^{-1} in the deepest layer from 30 to 45 cm depths. From this example one could conclude that the shallowest sediments are the most efficient ones in term of nitrate removal. While removal activity is first declining with depths

it later increases again. This finding is consistent with the higher amplitudes of oxygen concentration in 45cm depths compared to 25 cm depths, also suggesting higher biotic activity at the deepest layer. Potential reasons for this pattern could be decreasing NO_3^- penetration with depth (lower uptake at the middle layer than the shallowest one) which is in the deepest parts counter balanced by increased residence time and stronger reducing conditions.

5. Conclusion and Outlook

The role of the hyporheic zone as a ~~hot spot~~hotspot for instream nutrient cycling is indisputable (Mulholland et al., 1997; Fellows et al., 2001; Fischer et al., 2005; Rode et al., 2015). The loss of this essential function may be crucial under anthropogenic forcing, such as morphological alteration (Borchardt and Pusch, 2009), eutrophication (Ingendahl et al., 2009) and sediment loading (Hartwig and Borchardt, 2015). In all these cases, mass transfer to the hyporheic zone may be the rate limiting step for nutrient removal (Basu et al., 2011).

Despite decades of research on hyporheic nutrient cycling, robust quantitative data on horizontal nutrient fluxes through the hyporheic zone are limited, which is mainly due to methodological constraints in measuring nutrient concentrations and water flux in the subsurface of streams (O'Connor et al., 2010; Boano et al., 2014; Gonzalez-Pinzon et al., 2015).

Passive flux meters have the potential to fill the gap in measured quantitative nutrient fluxes to the reactive sites in the sediments of rivers. Up to date, ~~this is~~HPFM are virtually the only method which can simultaneously capture nutrient and water flux through hyporheic zone within the same device and at the same spatial location. The ~~successful~~ field testing of several devices proved ~~their~~the general applicability of passive flux meters for quantifying NO_3^- and PO_4^- flux to reactive sites in the hyporheic zone. ~~Hyporheic~~The hyporheic flux rates of nutrients and denitrification rates measured in an agricultural 3rd order stream were generally in agreement with ~~contemporary alternative measurements and~~ rates reported in the literature. Our results clearly highlight the advantages of HPFM compared to commonly used methods~~,~~ (i.e. grab sampling of pore water and separate measurements of hyporheic exchange and Darcy velocities), first of all ~~their capability~~the capacity to integrate over longer time ~~spans~~periods.

Quantifying nutrient flux to the potentially reactive sites in the hyporheic zone is an essential step to further improve our process based knowledge on hyporheic nutrient cycling. In the future, long-term measurements of nutrient fluxes as obtained from HPFM can feed into and advance the transport part of nutrient cycling models.

We anticipate further improvement and increased use of ~~hyporheic zone~~ passive flux meter approaches in order to advance conceptual models of nutrient cycling in the hyporheic zone. We demonstrated modifications which extended PFM application from groundwater to hyporheic zones. ~~Taking a similar approach, passive flux meters may be adapted~~Current limitations related to the potential bias of results due to biofilm growth on sorbents require further analysis for the ~~use in other environments: e. g. lakes, estuaries, etc.~~identification of more suitable sorbents.

While we focused on nutrients, ~~PFMs~~PFM may also be used for a wide range of other substances like contaminants or trace elements. ~~Their deployment should be considered whenever~~

~~flux instead of concentration is needed~~

~~the focus is on general transport characteristics of a stream rather than short term dynamics,~~

~~the use of sensors is impractical because sensors for the target solute are not available, or the hyporheic environment is not accessible with electronical sensors.~~

Being labor efficient and attractive with respect to relatively low costs, numerous HPFM can be efficiently used to cover larger areas and assess the degree of local heterogeneity. Further, neither ~~sensitive~~advanced technology, maintenance, ~~nor~~or power supply are needed which can be extremely advantageous for the use in remote areas or study sites without ~~power~~ infrastructure.

Acknowledgements

~~I~~We thank Uwe Kiwel for his technical support during the field work and Andrea Hoff and Christina Hoffmeister from the analytical department of the UFZ for their assistance in the laboratory experiments. ~~I am~~We are also grateful for the fruitful discussions with James Jawitz, Andreas Musolff, Christian Schmidt and Nico Trauth.

Figures and tables

Table 1. ~~**Resident Tracers and Partitioning Characteristics**~~ **Resident tracers per liter of aqueous solution and their partitioning characteristics. Retardation factors (R_d) for the specific set of tracers and AC used in this study had previously been determined by Cho et al. (2007)**

Resident tracers	Aqueous concentration ($g\ L^{-1}$)	Rd
methanol	1.2	4.9
ethanol	1.2	20
Isopropyl alcohol (IPA)	2.3	109
tert-butyl alcohol (TBA)	2.3	309
2,4-dimethyl-3-pentanol (DMP)	1.2	>1000

Table 2. Selected morphological and hydrological parameters of the testing site~~. All parameters are averages~~ for the duration of the testing phase from 04.06.2015-11.06.2015. Ranges are indicated for directly measured parameters, the remaining parameters have been calculated from listed means. HZ= Hyporheic zone

Surface water	acronym	unit	mean	range
cross sectional area	A_{SW}	m²	3.41	
depth ~~(mean)~~	h	m	0.565	0.54 - 0.61
width ~~(mean)~~	w	m	6.03	5.57 - 6.29
mean velocity	v	m s^{-1}	0.097	
discharge	Q_{SW}	m^3 s^{-1}	0.32	0.30 - 0.34
NO_3^- ~~N~~ concentration	$C_{NO3\ SW}$	mg ~~m~~ $^{-3}L^{-1}$	~~2863~~2.86	2.16 - 3.26
NO_3^- ~~N~~ mass flux	~~M~~ $_{NO3}M_{NO3\ SW}$	mg s^{-1}	896	
PO_4^--P	$C_{PO4\ SW}$	mg ~~m~~ $^{-3}L^{-1}$	0.165	0.111 - 0.231
PO_4^--P mass flux	$M_{PO4\ SW}$	mg s^{-1}	51	
Hyporheic zone upper 50cm	-			
Assessed depth of HZ ~~assessed with HPFM~~	h_{HZ}	m	0.5	
cross sectional area of HZ	A_{HZ}	m²	3.02	

Gelöschte Zellen
Eingefügte Zellen
Eingefügte Zellen
Gelöschte Zellen
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Table 3. Summarized parameters of NO_3^- transport and removal through the upper 50 cm of the hyporheic zone at the test site~~. Values are averages~~ for the testing phase from 04.06.-11.06.2015. Ranges are indicated for directly measured parameters, the remaining parameters have been calculated from listed means.

~~parameter~~	~~token~~acronym	unit	mean	range
water flow through HZ	Q_{HZ}	L s^{-1}	0.0265	
% of river water entering HZ	~~% water HZ~~Q_{HZ}	%	0.008	
Horizontal Darcy velocity	q_x	cm d^{-1}	76	20 - 116
average NO_3^- concentration in the HZ	$C_{NO3\ HZ}$	mg ~~m^{-3}~~L^{-1}	~~1389~~1.39	0.31 - 2.86
% NO_3^- entering the HZ which is denitrified	~~% denitri in HZ~~R_N	%	52	
potential NO_3^- load entering HZ	$M_{HZ\ theory}$	mg s^{-1}	0.08	
NO_3^- load measured in HZ	$M_{HZ\ measured}$	mg s^{-1}	0.037	

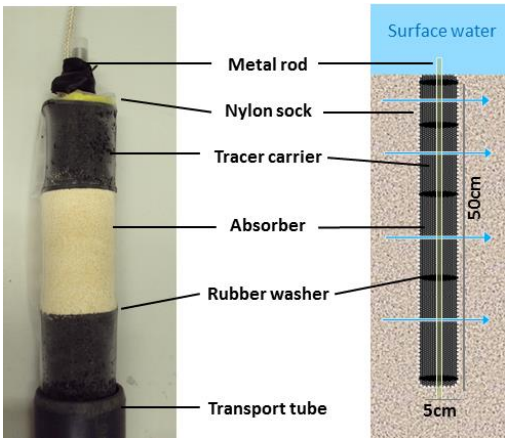

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Table 4. Benchmark surface water parameters derived from the continuous sensor records from 04.06.-11.06.2015 and 08.10. – 11.10.2015: Temp= temperature, SpC=specific conductivity, O_2 =dissolved oxygen

		Temp	SpC	pH	O_2	NO_3^-
		°C	µS cm^{-1}	-	mg L^{-1}	mg L^{-1}
04.-11. June 2015	mean	17.81	1063	8.42	9.37	2.86
	STD	2.57	46	0.27	2.01	0.32
	min	13.38	886	7.75	6.13	2.16
	max	23.79	1224	8.84	13.12	3.26
08.-11. Oct 2015	mean	11.22	951	8.21	10.48	2.75
	STD	2.75	59	0.10	0.91	0.28
	min	6.02	818	7.99	9.09	1.95
	max	15.32	1056	8.44	12.44	3.40

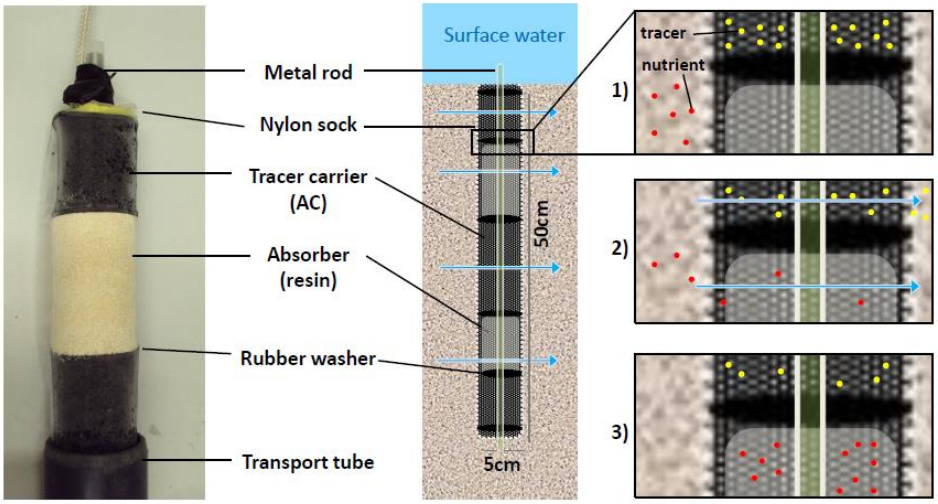


Figure 1. Photograph of an HPFM with alternating segements before deployment (left) ~~and~~, schematic profile of a deployed HPFM (middle) and schematic steps of HPFM functioning (right~~)~~): 1) directly after installation, tracer resides on activated carbon (AC), 2) infiltrating water washes out the tracer, nutrients enter the HPFM and are absorbed on the resin, 3) after retrieval nutrients are fixed on the resin, tracer concentration is diluted.

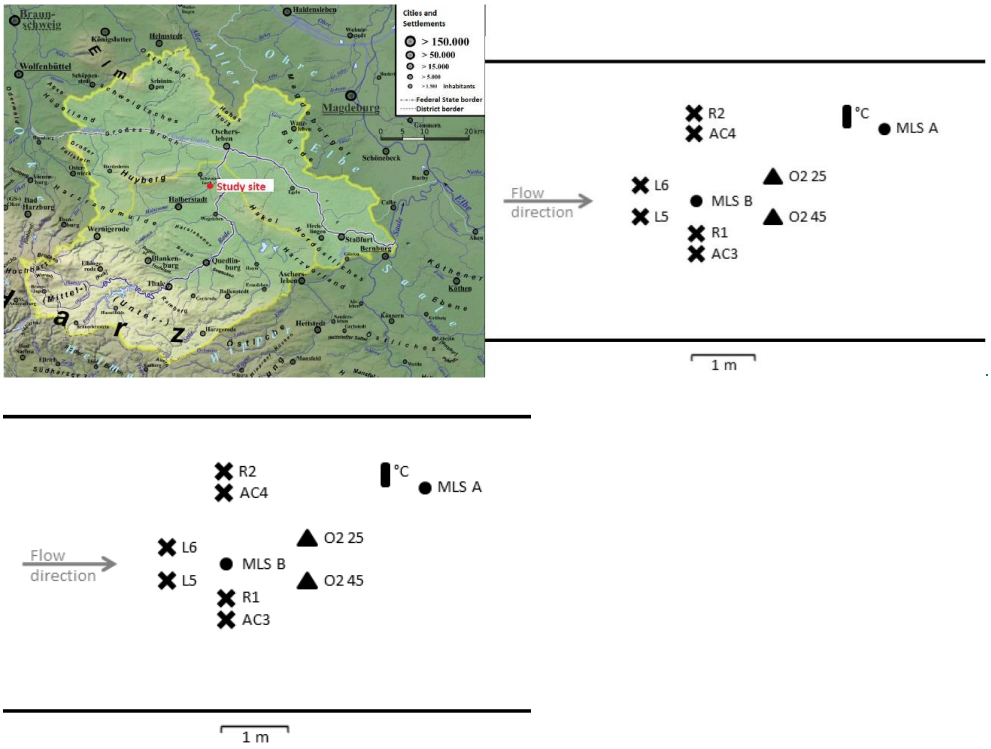
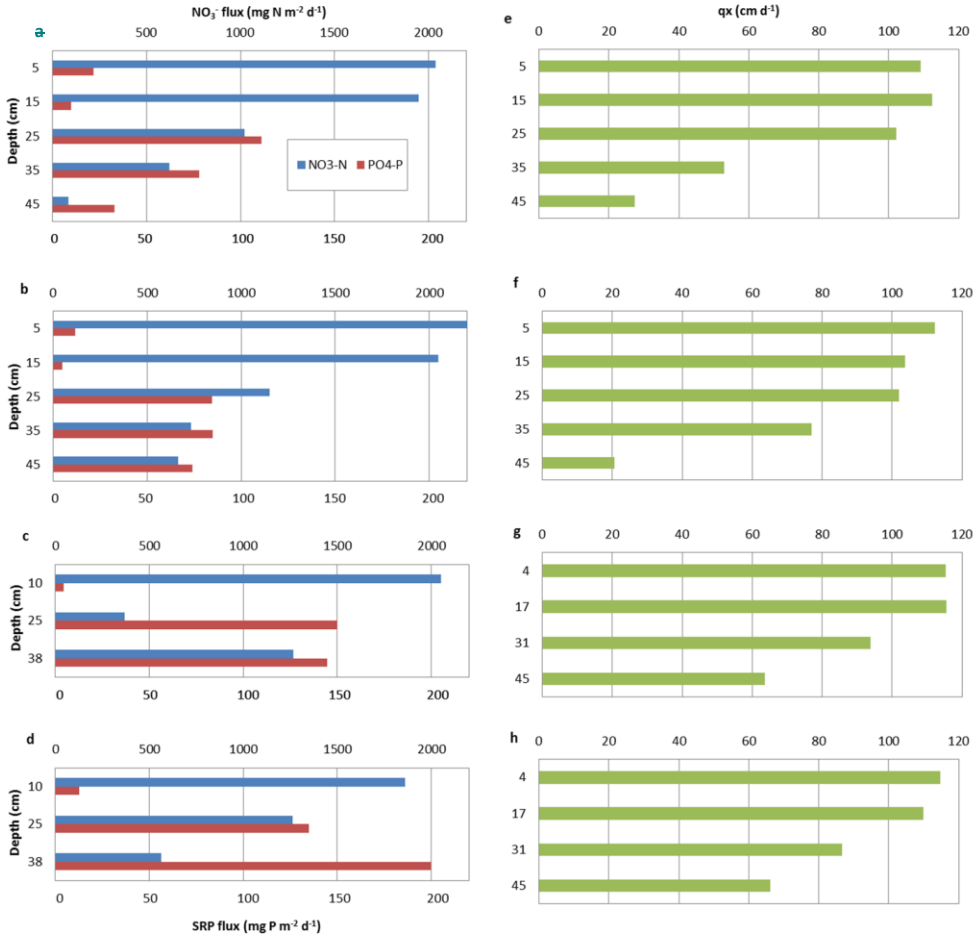


Figure 2. ~~**Map of Bode catchment, the study site is marked in red (left) and overview of**~~**Overview of the instrumental setup at the Holtemme for the testing phase in June 2015** ~~**(right).**~~**.**

R1, R2 resin only ~~**HPFMs**~~**HPFM; AC3, AC4 activated carbon only** ~~**HPFMs**~~**HPFM; L5,L6 alternating layered HPFMs; MLSA, MLSB Multi-level sampler; O2 25, O2 45 subsurface oxygen logger; °C vertical temperature profile**


a
NO_3^- flux (mg N m^{-2} d^{-1})
Depth (cm)
NO3-N
PO4-P
b
c
d
SRP flux (mg P m^{-2} d^{-1})
e
qx (cm d^{-1})
f
g
h

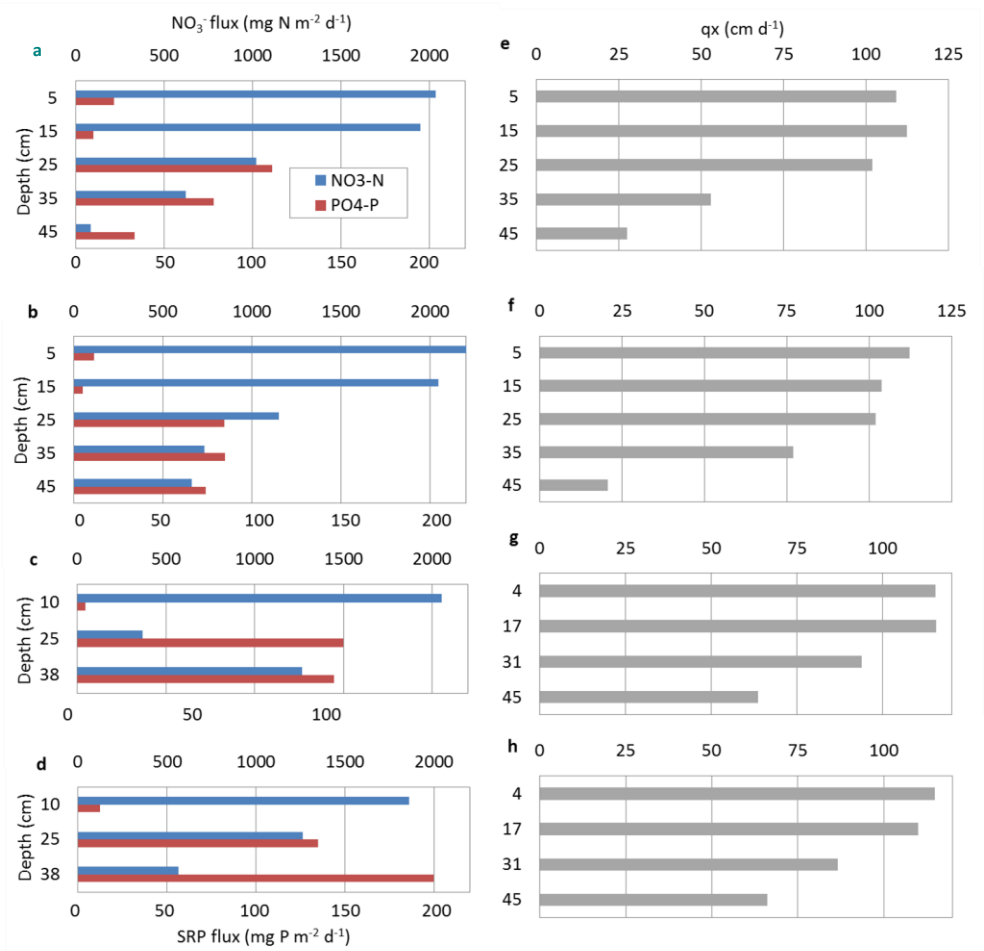


Figure 3. Time integrative measurements for the 04.-11.06.2015. Left side: Horizontal NO_3^--N and SRP-P flux in mg m^{-2} d^{-1} through the resin ~~HPFMs~~HPFM R1 (a), R2 (b) and the layered ~~HPFMs~~HPFM L5 (c) and L6 (d). Right side: corresponding Darcy velocities q_x in cm d^{-1} through the activated carbon ~~HPFMs~~HPFM AC3 (e) and AC4 (f) and the layered HPFMs 5L (g) and 6L (h)

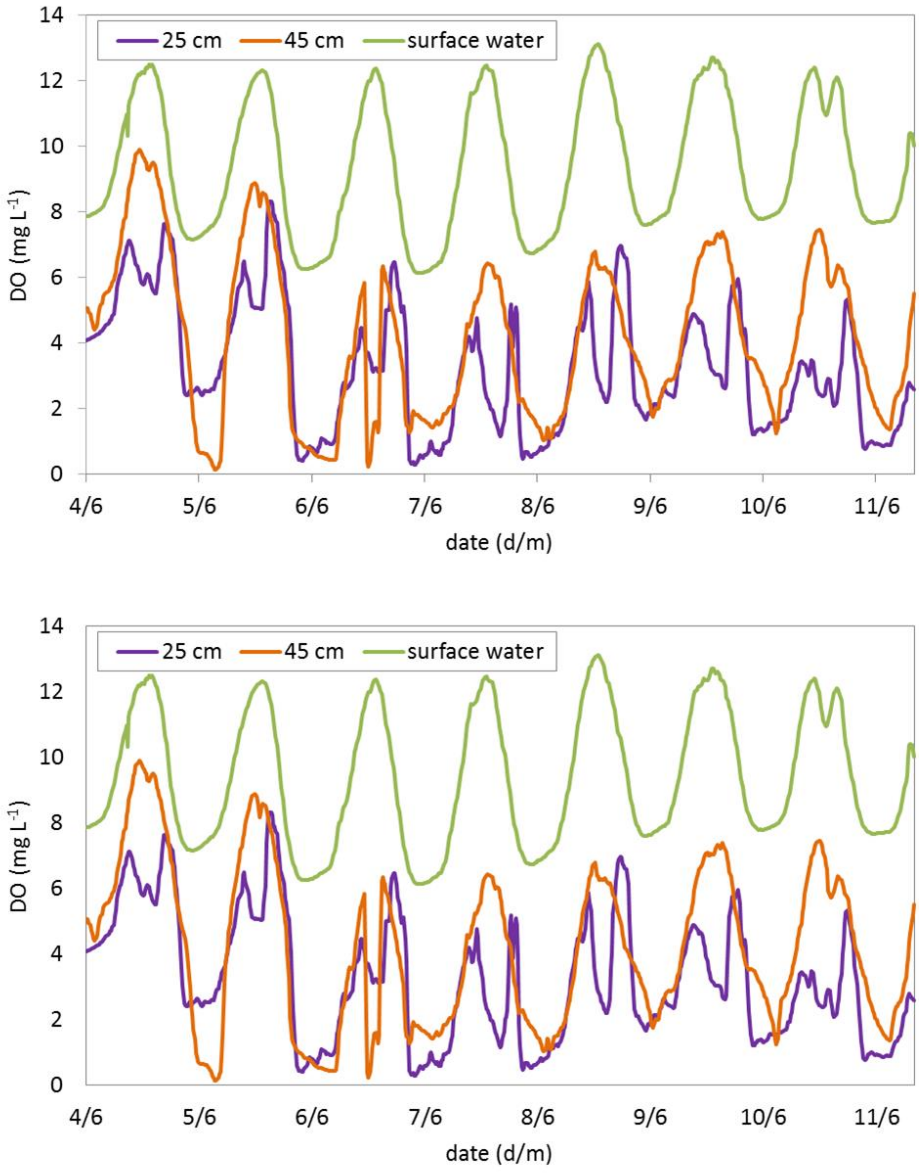
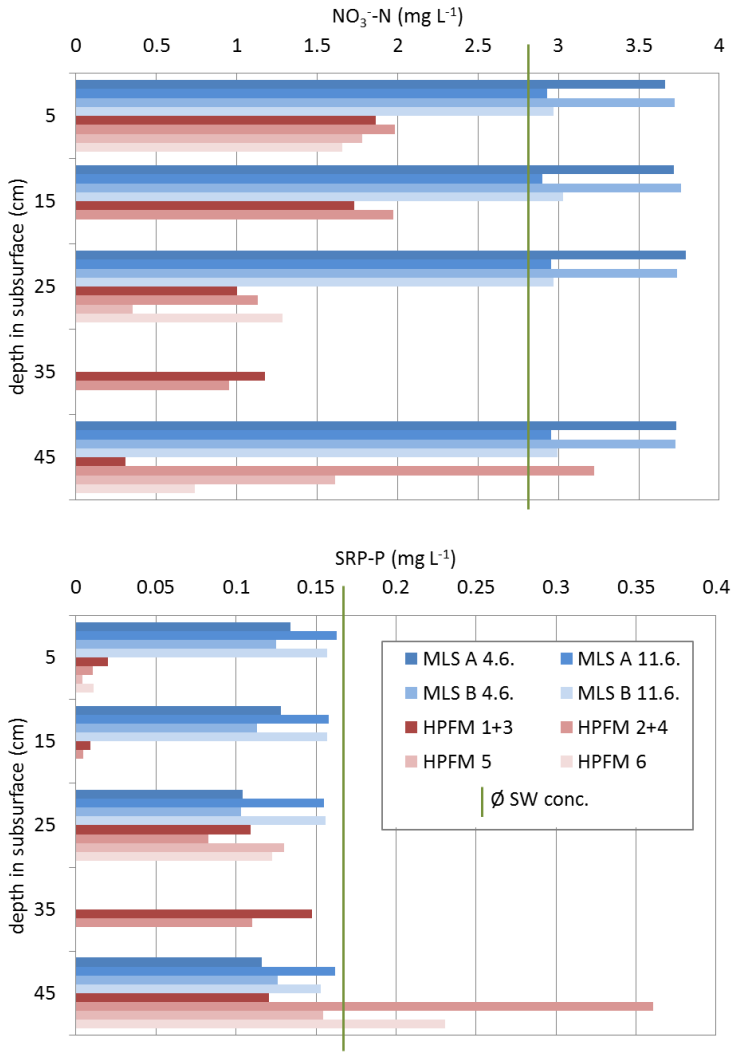


Figure 4. Time series of dissolved oxygen concentrations in the surface water (green) and the subsurface water (depth 25 cm, purple and depth 45 cm orange) at the study site from 04.-11.06.2015


NO3--N (mg L-1)
0
0.5
1
1.5
2
2.5
3
3.5
4
depth in subsurface (cm)
5
15
25
35
45
SRP-P (mg L-1)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
MLS A 4.6.
MLS A 11.6.
MLS B 4.6.
MLS B 11.6.
HPFM 1+3
HPFM 2+4
HPFM 5
HPFM 6
Ø SW conc.

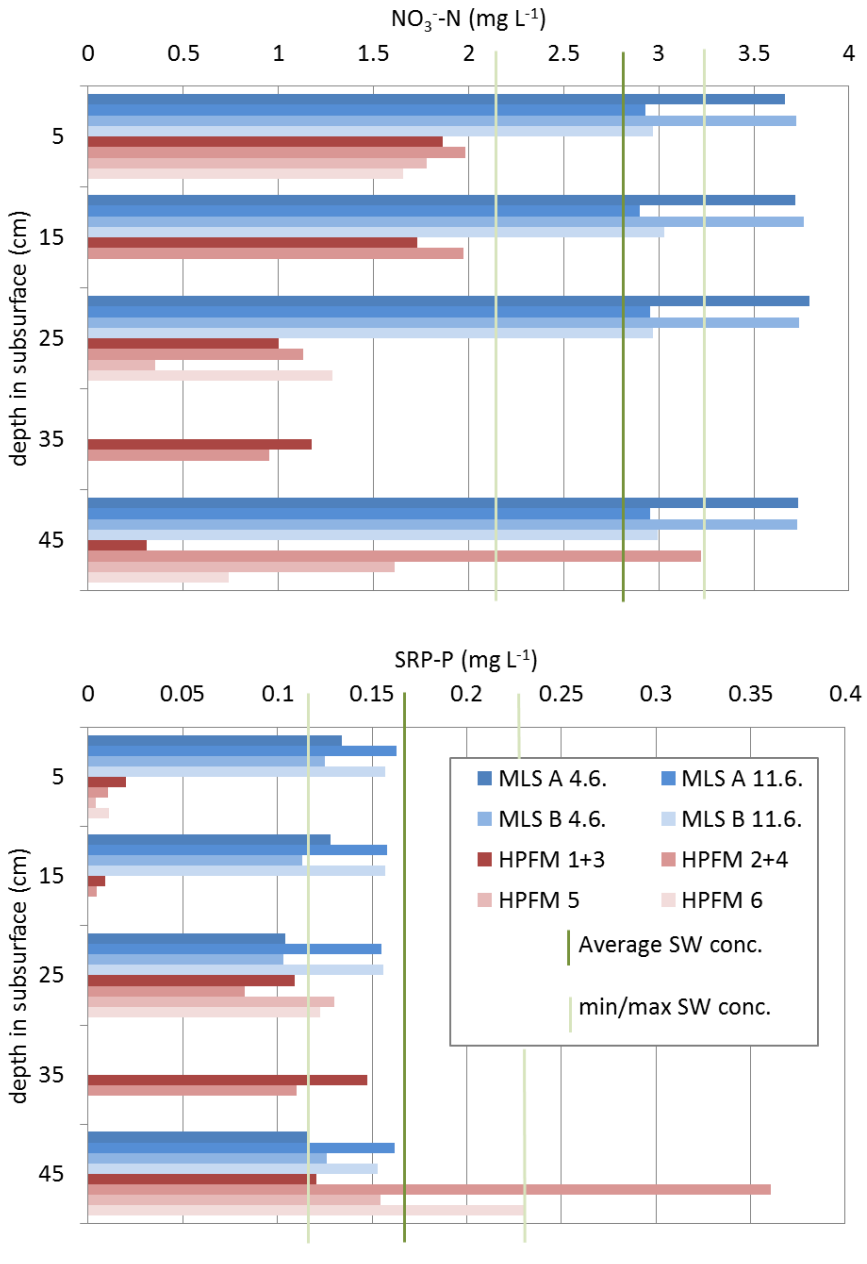

NO_3^--N (mg L^{-1})
0
0.5
1
1.5
2
2.5
3
3.5
4
depth in subsurface (cm)
5
15
25
35
45
SRP-P (mg L^{-1})
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
depth in subsurface (cm)
5
15
25
35
45
MLS A 4.6.
MLS A 11.6.
MLS B 4.6.
MLS B 11.6.
HPFM 1+3
HPFM 2+4
HPFM 5
HPFM 6
Average SW conc.
min/max SW conc.

Figure 5. Comparison between manually sampled pore water from MLS (red) and HPFM (blue) for NO_3^--N (top) and SRP-P (bottom). Each MLS was sampled on the 04. and 11.06.2015. Average surface water concentration during the deployment time is marked in green.

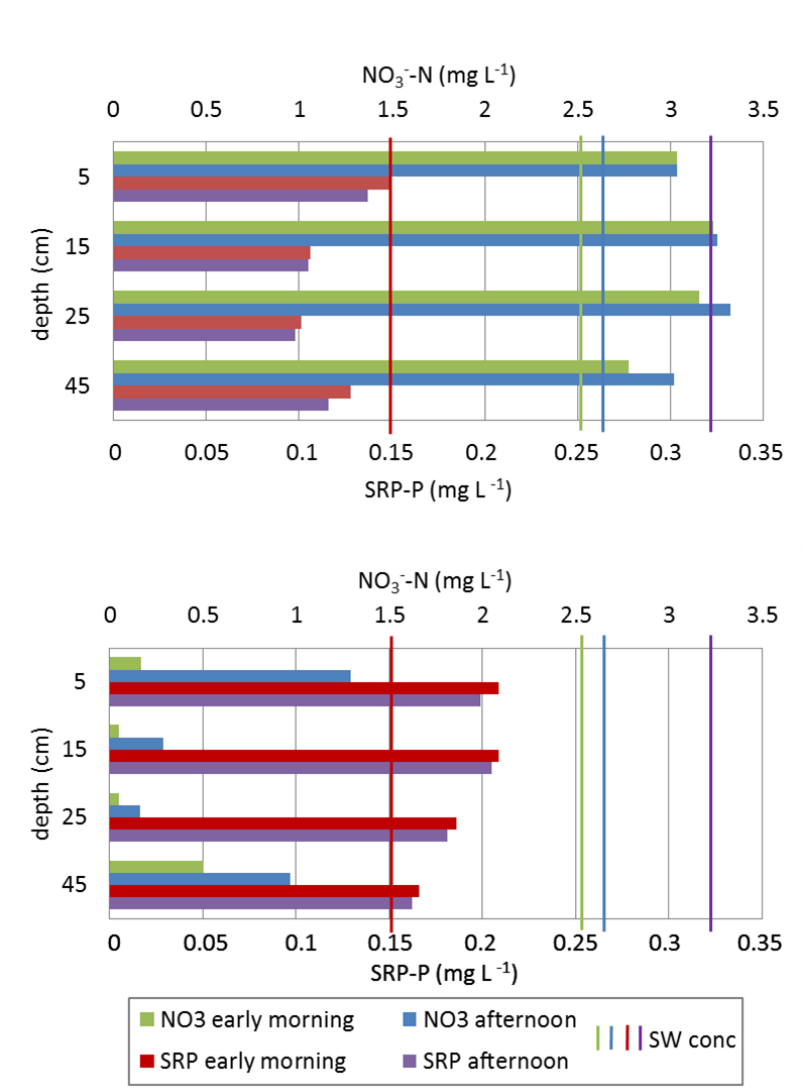


Figure 6. Concentrations of NO_3^--N and SRP in time differentiating manually taken pore-water samples from MLS A (bottom) and MLS B (top) on 8th October 2015. Corresponding surface water concentrations are marked as vertical lines.

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